Hydrogen and Electrical Energy Storage

20 March 2013

F.M. Mulder & M. Wagemaker
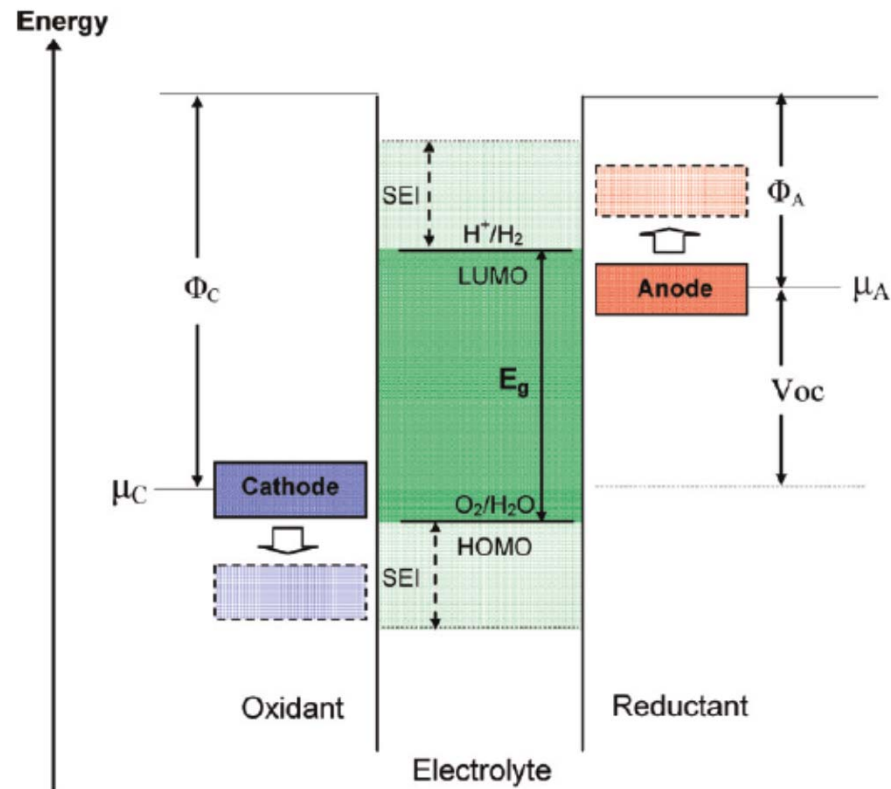
Radiation, Radionuclides and Reactors

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Program Batteries

Lecture 1:   History, Applications, basic Electrochemistry and thermodynamics
Feb 27   of batteries: Redox reactions, Gibbs free energy, chemical potential,
Nernst.

Lecture 2:   Solid state electrode reaction mechanisms, phase diagrams, phase rule,
March 6   Gibbs Free energy, voltage profiles, capacities and energy densities.
Li-ion batteries

Lecture 3:   Continue topics Lecture 2.
March 13   Electrolyte stability: Pourbaix diagram, band structure solids, Cycle life.

Lecture 4:   Kinetics, Buttler-Volmer, diffusion, solid state diffusion
March 20   Discussion on Science paper 6 seconds discharge.

Lecture 5:   Super capacitors
March 27   Future systems: Li-air, Li-sulphur
Flow-cells
Costs and Performance comparison batteries/systems
Material Abundance

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Electrolyte-electrode stability diagram

$$E_{Cell} = \phi_C - \phi_A = \mu_{e^-}^A - \mu_{e^-}^C = \varepsilon_F^A - \varepsilon_F^C$$

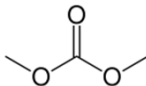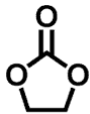**T**U Delft

Example SEI Formation: Graphite
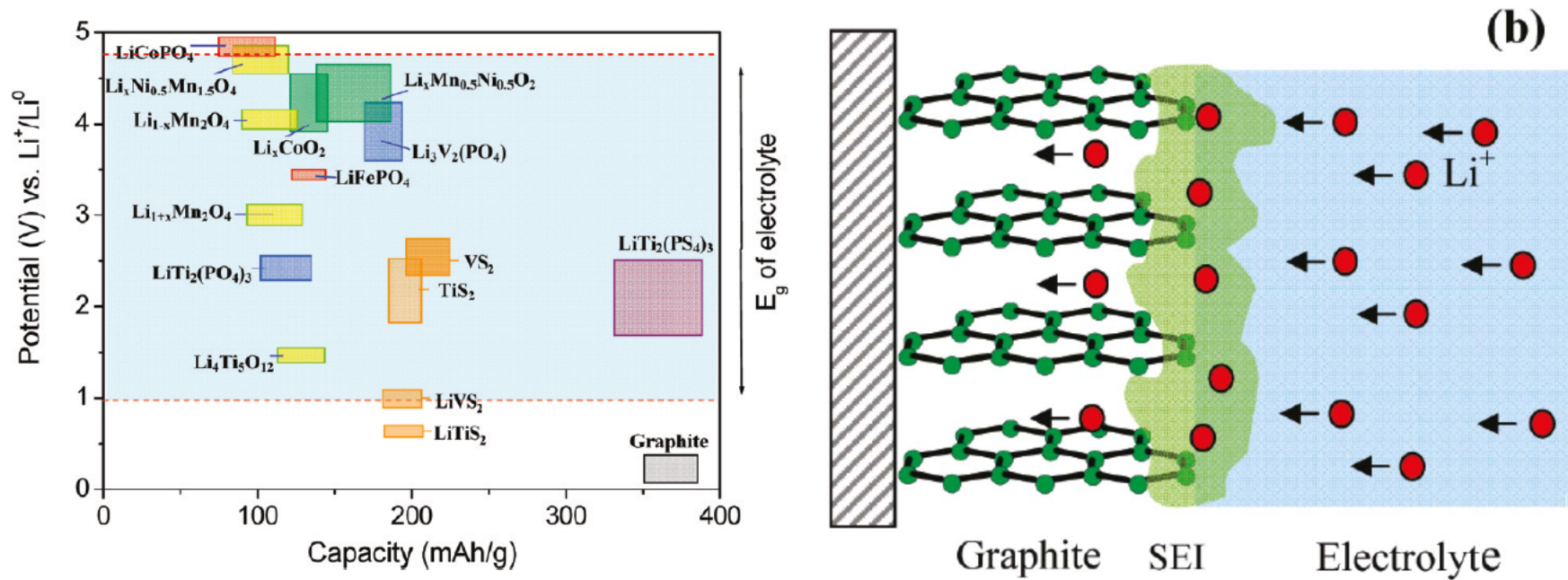
Demands Li-ion Electrolyte

- **Good (Li⁺) ionic conductor**
- **Electronic Isolator**
- **Stability window 5 V (depends on sys.)**
- **Stable up to ~ 70 degree celcius**
- **Cheap**
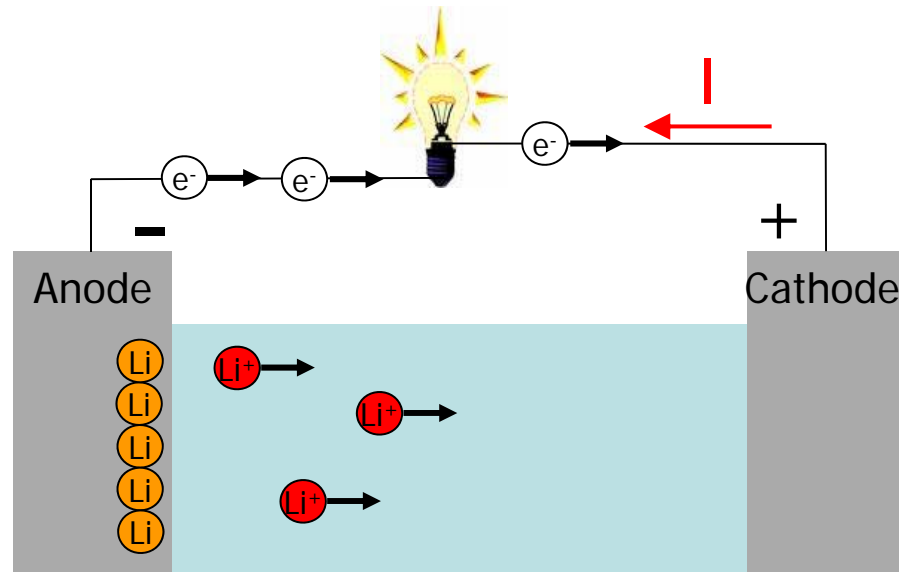- **Non toxic**

Mostly applied: Non aqueous solvents:

Ethylene Carbonate (EC), Dimethyl Carbonate (DMC)

Good ionic conduction, stability ~ 0.8-4.5 V (vs Li/Li⁺)

Medium toxic, flammable, unstable etc -> Casing battery should be very good (=expensive)
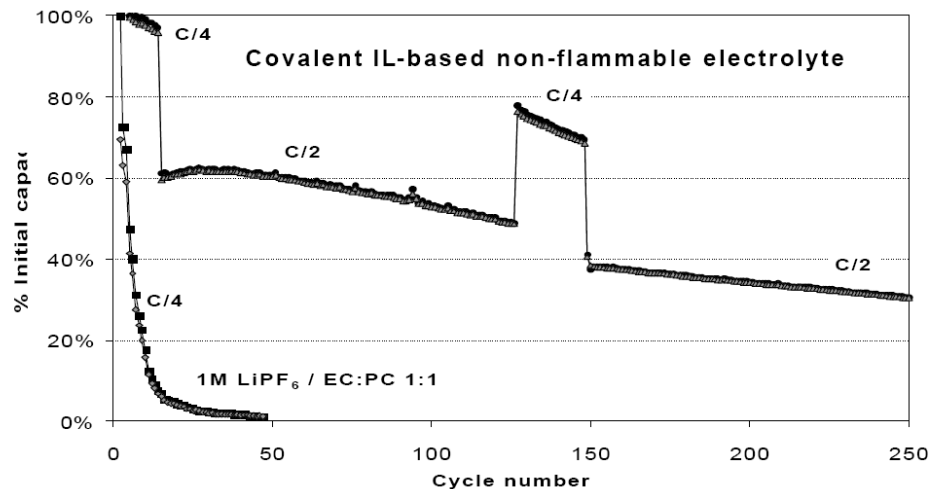Li salts: $LiClO_4$ or $LiPF_6$: Toxic and expensive

Li-ion batteries, ionic liquids

Ionic liquid: salt in the liquid state: electronic isolator
good ionic conductor
thermal stability
non-flammable   } safe
chemically stable (large stability window)
cheap?

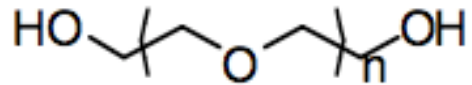## Li-ion Cycling Performance at 100°C

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Li-ion batteries, solid electrolytes

Solid electrolytes:

Less difficulty/cost associated with long term encapsulating liquid electrolytes (that may start leaking), freedom design of batteries, high temp.

Example: polymer electrolytes like polyethyleneoxide

Because polymers can have intrinsic mobility of the polymer chains, a dissolved Li salt can also move through it. However, solid electrolytes show much lower Li^+ conductivities (low power density)

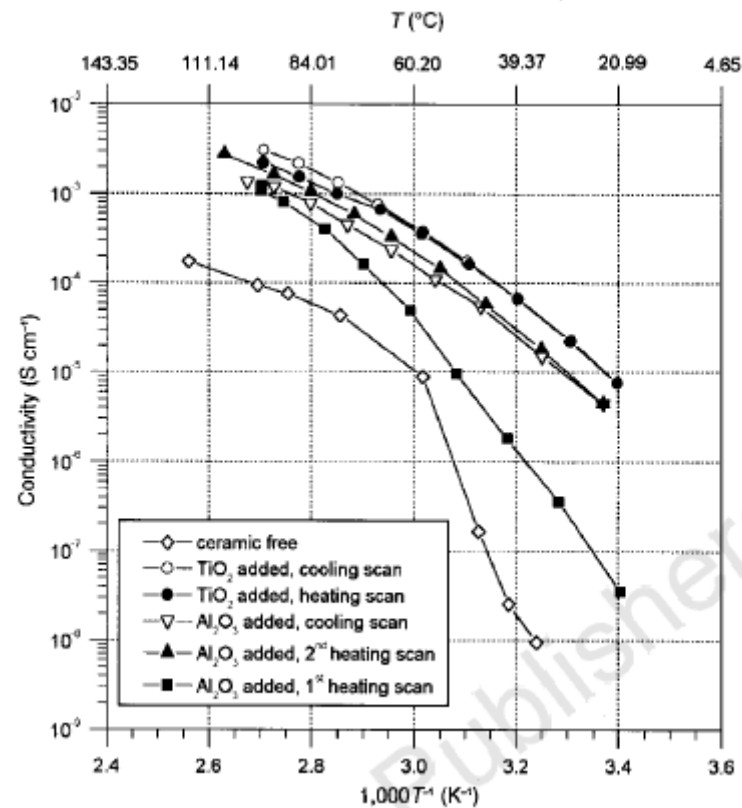Application limited to large systems that can be maintained at high temperatures

Poor ionic mobility, PEO LiI

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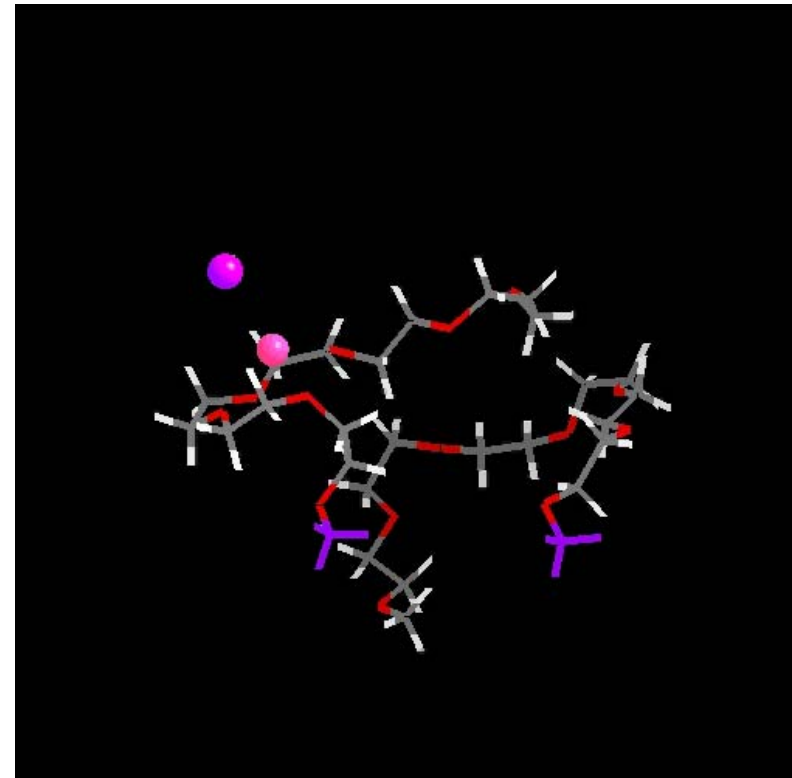
Li-ion batteries, electrolytes

Other strategy:

Adding nano-particles increases the
Conductivity in PEO-LiClO$_4$

Space charges

Two ion conductors and poor electronic isolators:

$\mu_A > \mu_B$

$\bar{\mu}_A = \bar{\mu}_B$
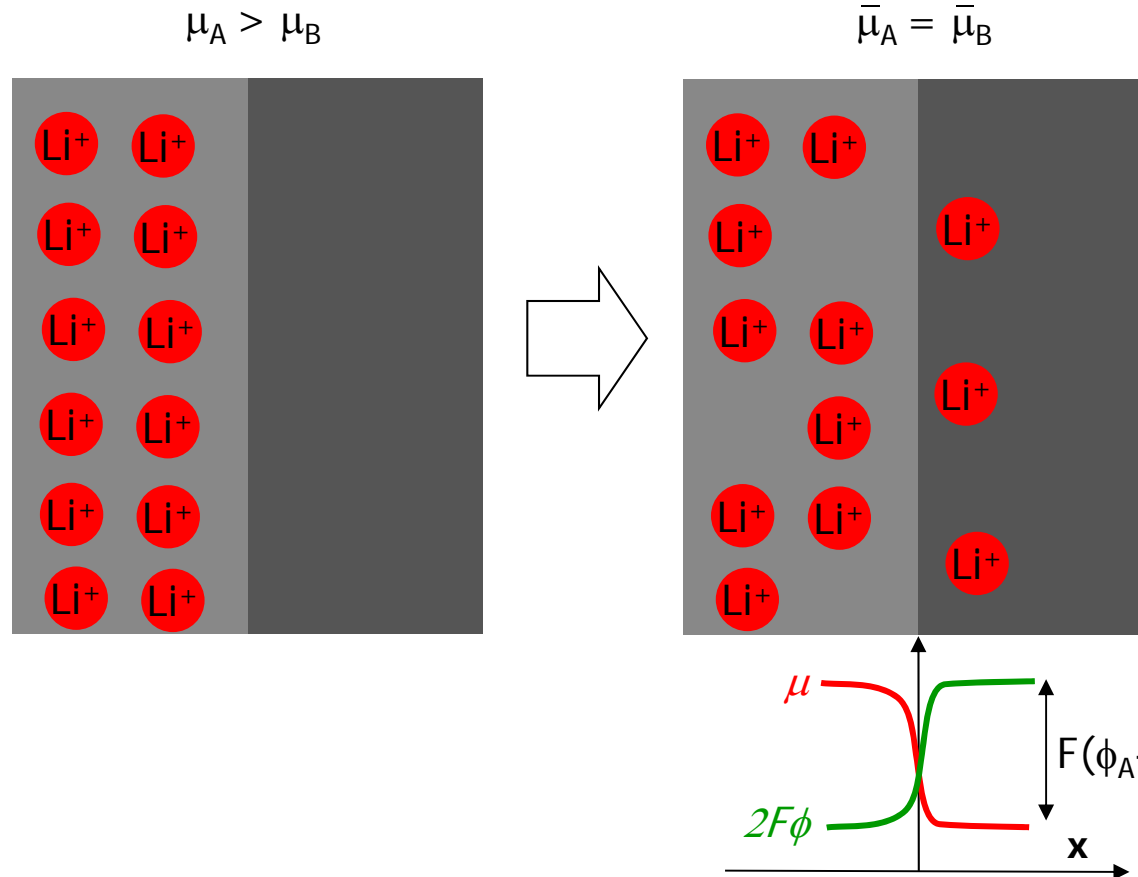
$$\left(\phi_A - \phi_B\right) = -\frac{\left(\mu_A - \mu_B\right)}{F}$$

$$\mu_A + F\phi_A = \mu_B + F\phi_B$$

$$\bar{\mu}_A = \bar{\mu}_B$$

Creates vacancies in A!

Is called "Space Charge"

$F(\phi_A-\phi_B)=-(\mu_A - \mu_B)$

μ

$2F\phi$

x

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For diffusion you need vacancies

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Li-ion batteries, electrolytes
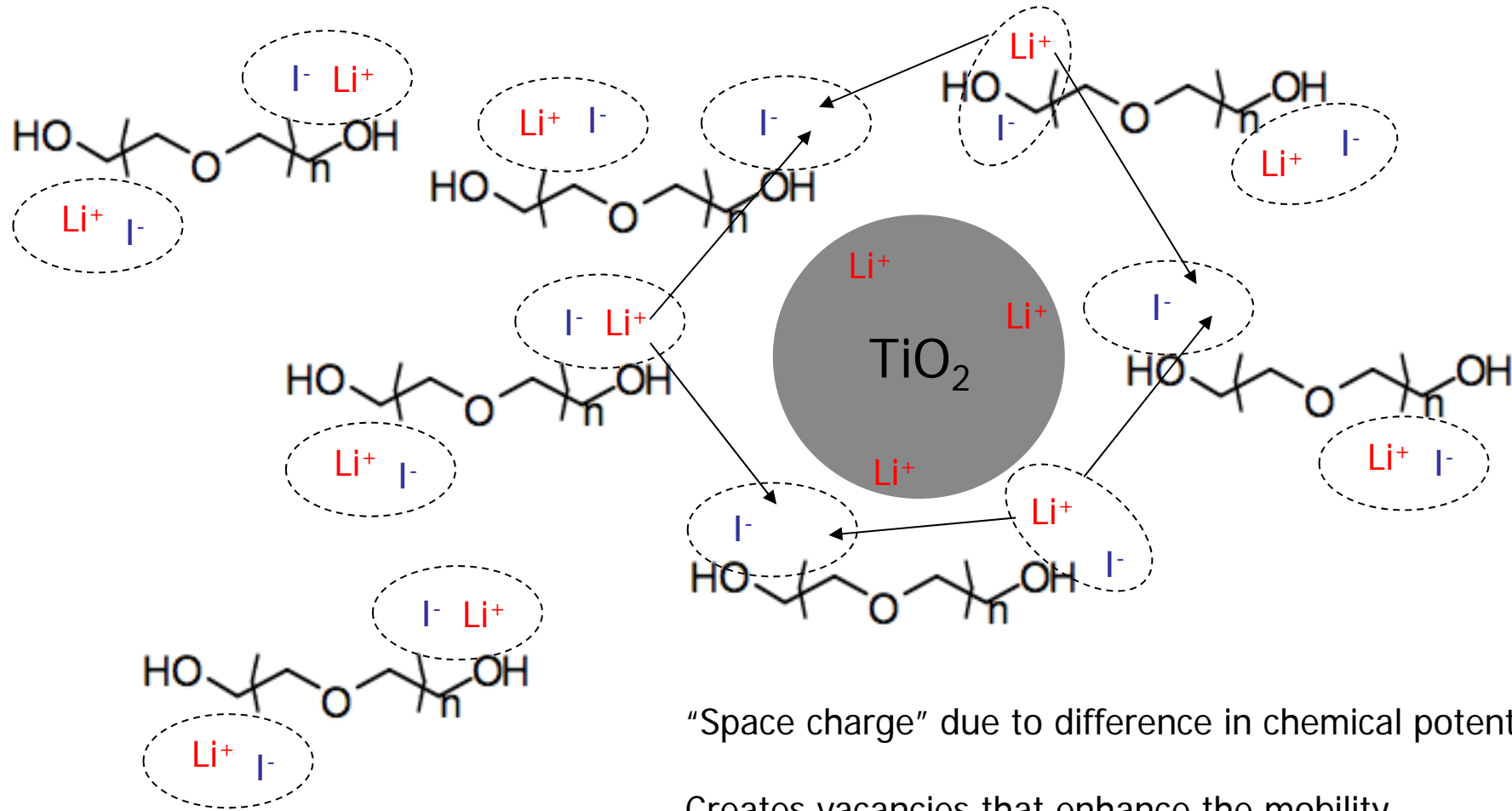
"Space charge" due to difference in chemical potential

Creates vacancies that enhance the mobility

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Home assignments

Read Chapters 3.1-3.3 Electrochemistry

Read Paper Ceder et al. Science

Exercise:
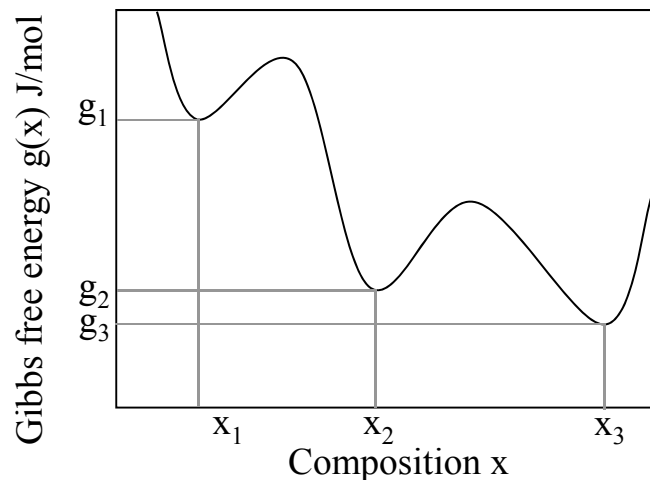
g(x) is the Gibbs Free energy of the cathode during discharge, assume the potential of the anode to be 0 and constant

a) Sketch the voltage profile resulting from the Gibbs Free energy diagram
b) In which direction with this reaction proceed
c) Calculate the voltage of the voltage plateau('s) if any.
d) Sketch a phase diagram that could represent this Gibbs Free energy diagram

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Home assignment

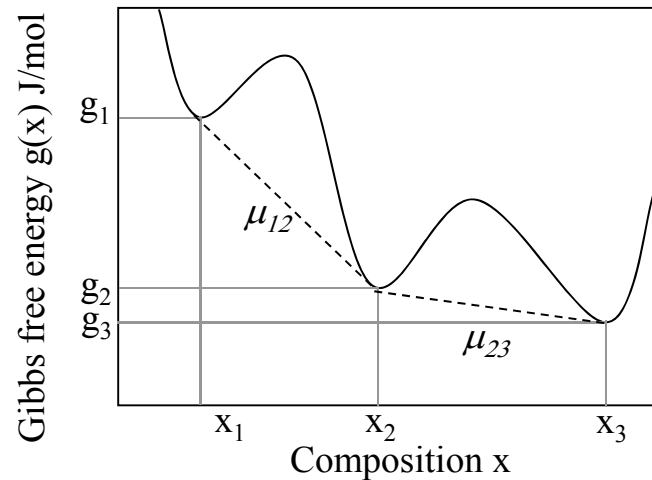g(x) is the Gibbs Free energy of the cathode during discharge, assume the potential of the anode to be 0 and constant
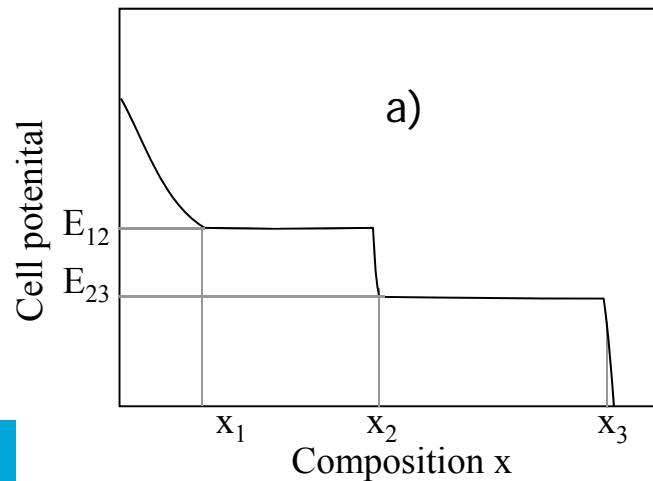
a) Sketch the voltage profile resulting from the Gibbs Free energy diagram
b) Which direction will this reaction proceed?
c) Calculate the voltage of the voltage plateau('s) if any.
d) Sketch a phase diagram that could represent this Gibbs Free energy diagram

b) In the direction of decreasing Gibbs Free energy: right

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Home assignment
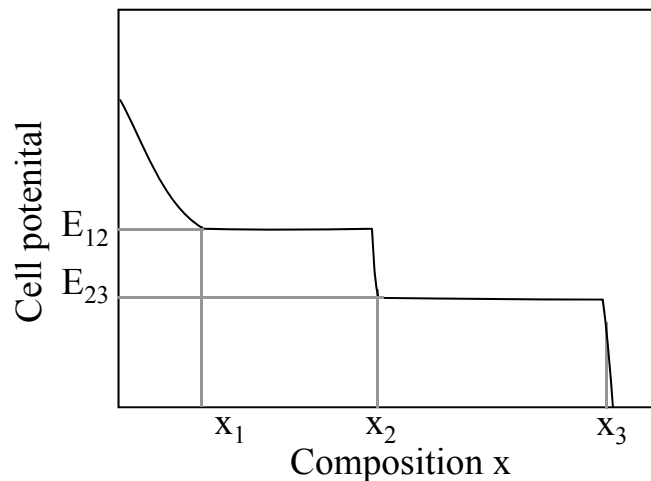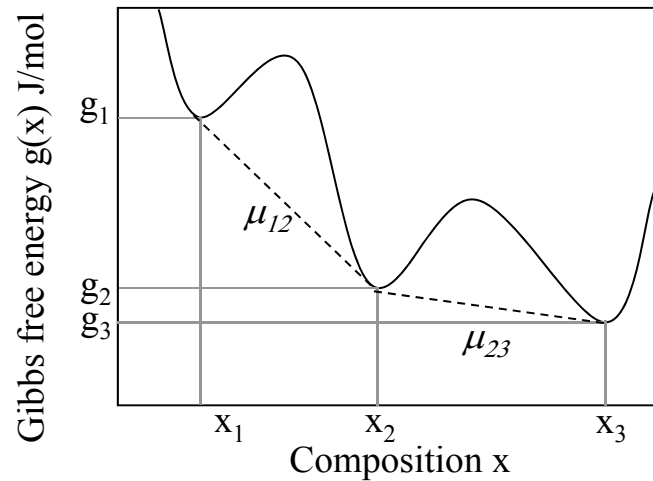
c)
$$g(x)^{1,2}_{\text{common-tangent}} = \frac{g_2 - g_1}{x_2 - x_1} x + C_{12}$$

$$\mu_{12} = \frac{\partial g}{\partial x} = \frac{g_2 - g_1}{x_2 - x_1} = \text{constant} \ (x_1 < x < x_2)$$

$$E_{12} = -\frac{\mu_{12}(x) - \mu_{Anode}}{zF} = \frac{g_1 - g_2}{F} \ (x_1 < x < x_2)$$

$$E_{23} = -\frac{\mu_{23}(x) - \mu_{Anode}}{zF} = \frac{g_2 - g_3}{F} \ (x_2 < x < x_3)$$

d)
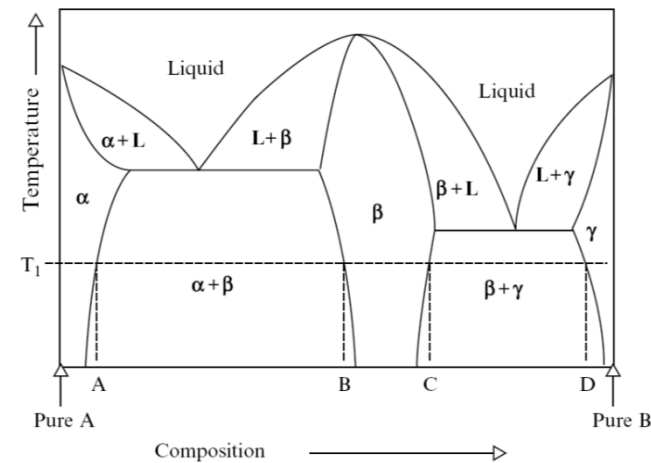
Kinetics in batteries
Charge transport

Charge transport, kinetics
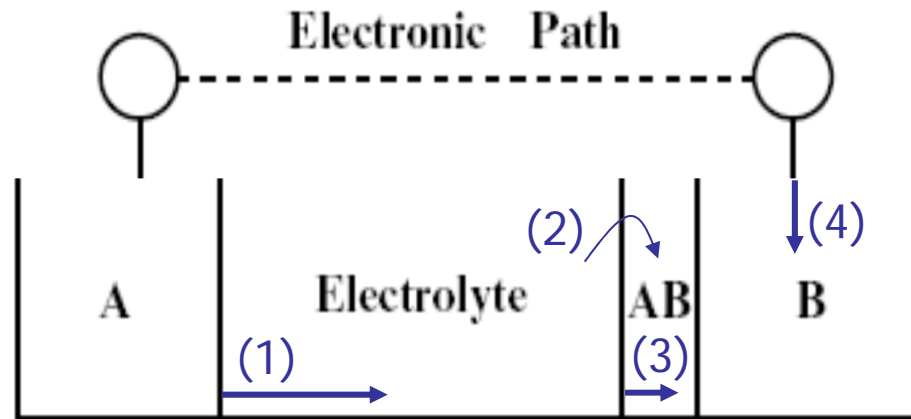
(1) ionic conduction A$^+$
(2) Charge transport over the electrolyte-electrode interface
(3) ionic conduction A or B
(4) electronic conduction

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Question kinetics 1

If the charge transport kinetics is improved:

a) The power density will improve

b) The energy density will improve

c) Both power and energy density will improve

d) No clue

$$EnergyDensity[J / g] = \frac{xzF\varepsilon_{Cell}}{M} = capacity \times \varepsilon_{Cell} \quad [C/g \times V]$$

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Question Energy Density

26 Why do you think batteries have in practice relatively thin electrodes?

a) Difficult to make

b) Long (dis)charge times

c) Shorter cycle life

d) No clue

$\sim 300\ \mu m$

L: diffusion length:
D: diffusion coefficient
t: diffusion time

$$L \approx \sqrt{\pi D t}$$

$$t \approx \frac{L^2}{\pi D}$$

Electrode 6 times thicker => takes 36 times longer to charge

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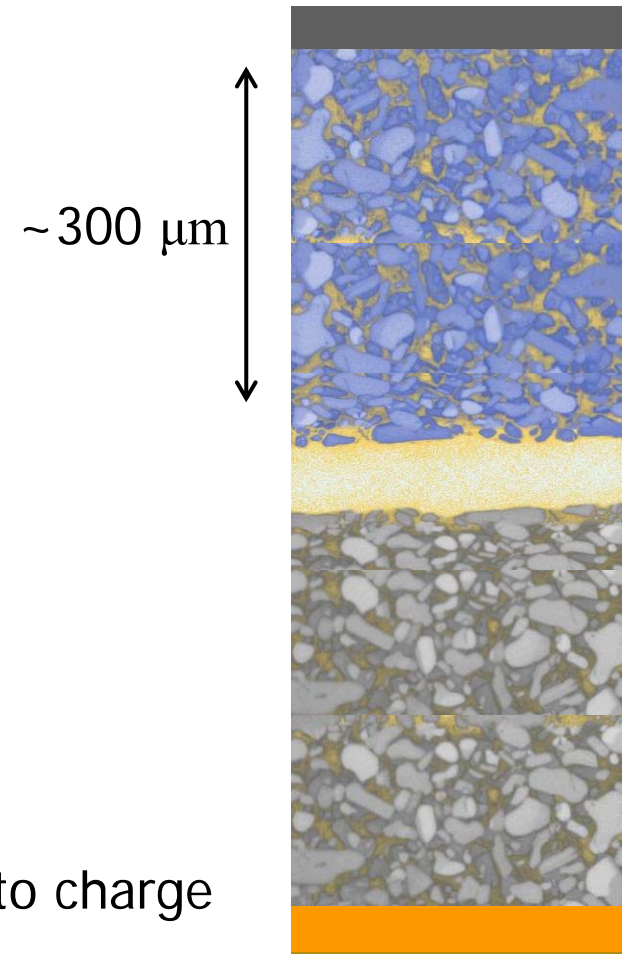
Question kinetics 2
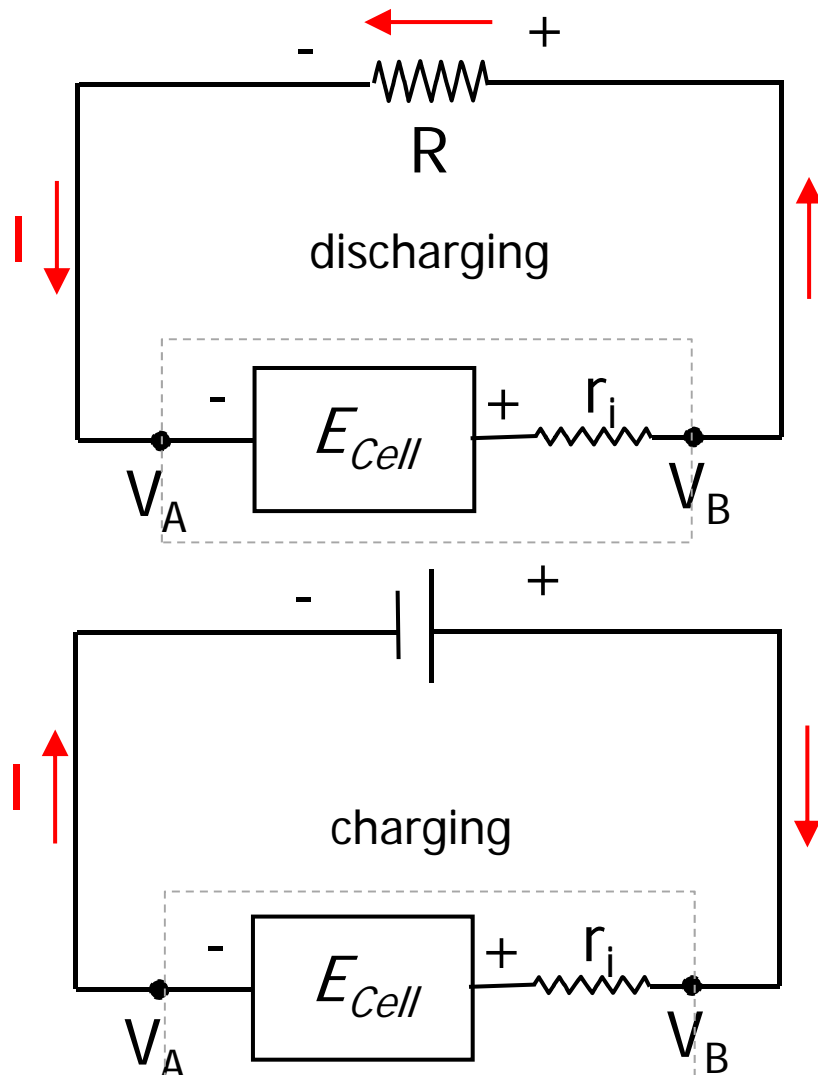
Up till now we assumed no current was running, resulting in the open cell potential (Equilibrium Thermodynamics).

$$R = \infty, I = 0: \quad V_{Battery} = V_B - V_A = E_{Cell}$$

What is the consequence of the internal resistance during <u>discharge</u> on V_B-V_A (the measured voltage over the battery)?
a) V_B-V_A increases
b) V_B-V_A decreases
c) V_B-V_A remains constant
d) No clue

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Internal resistance
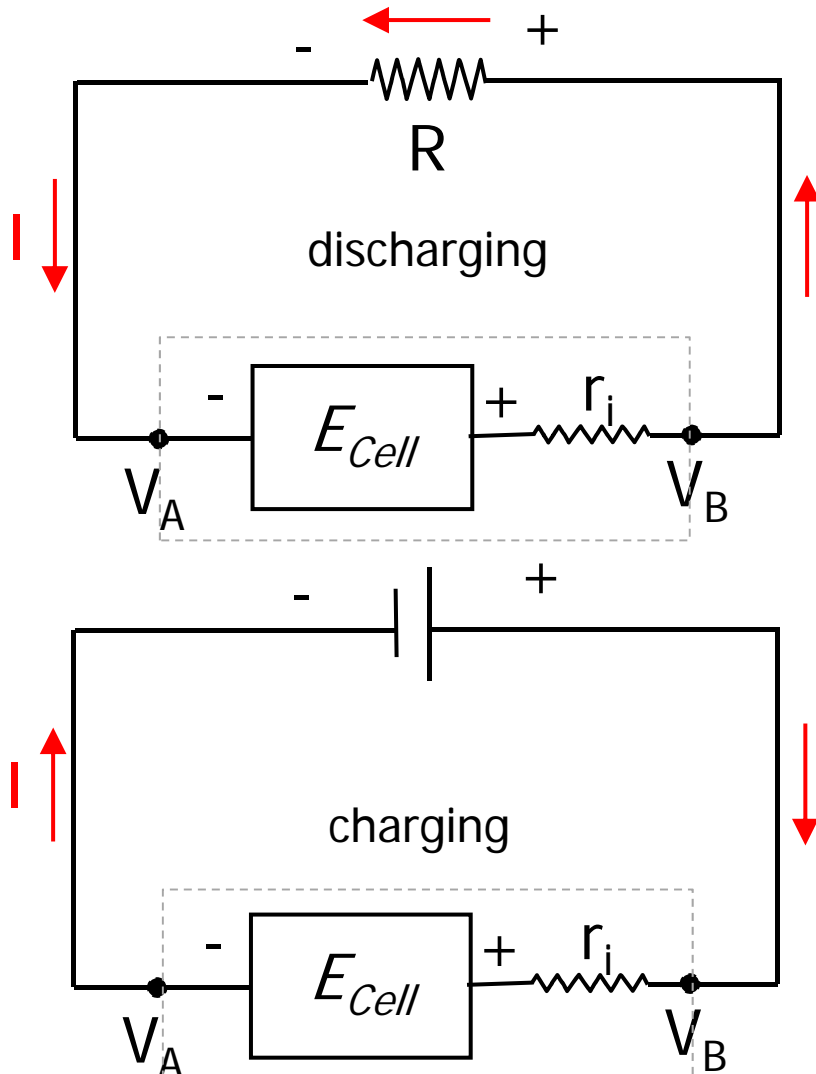
Up till now we assumed no current was running, what is the consequence of that?

Equilibrium:

$$R = \infty, I = 0: \quad V_{Battery} = E_{Cell}$$

Discharging:

$$V_B - V_A = V_{Battery} = E_{Cell} - Ir_i$$

$$V_{Battery} < E_{Cell}$$

Charging:

$$V_B - V_A = V_{Battery} = E_{Cell} + Ir_i$$

$$V_{Battery} > E_{Cell}$$

Definition overpotential or polarization: (deviation from equilibrium)

$$\eta = Ir_i$$

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Non-equilibrium electrochemistry

−

+

porous
barrier

Anode

e⁻
e⁻ Zn^{2+}

e⁻ Zn^{2+}
e⁻

e⁻ Zn^{2+}
e⁻

cathode

NO_3^- +
NO_3^- +
NO_3^- +
NO_3^- +
NO_3^- +
NO_3^- +

Non-Equilibrium: $\phi_A \leftarrow \phi_E$ $\phi_E \leftarrow \phi_C$

Equilibrium: $E_A = \phi_E - \phi_A = -\varepsilon_{Zn/Zn2+}$ $E_C = \phi_C - \phi_C = \varepsilon_{Cu/Cu2+}$

$\phi_A \leftarrow \phi_E$ $\phi_E \leftarrow \phi_C$

$$\varepsilon_{\text{Discharge}} = \phi_C - \phi_A < \varepsilon_{\text{Cell}}$$

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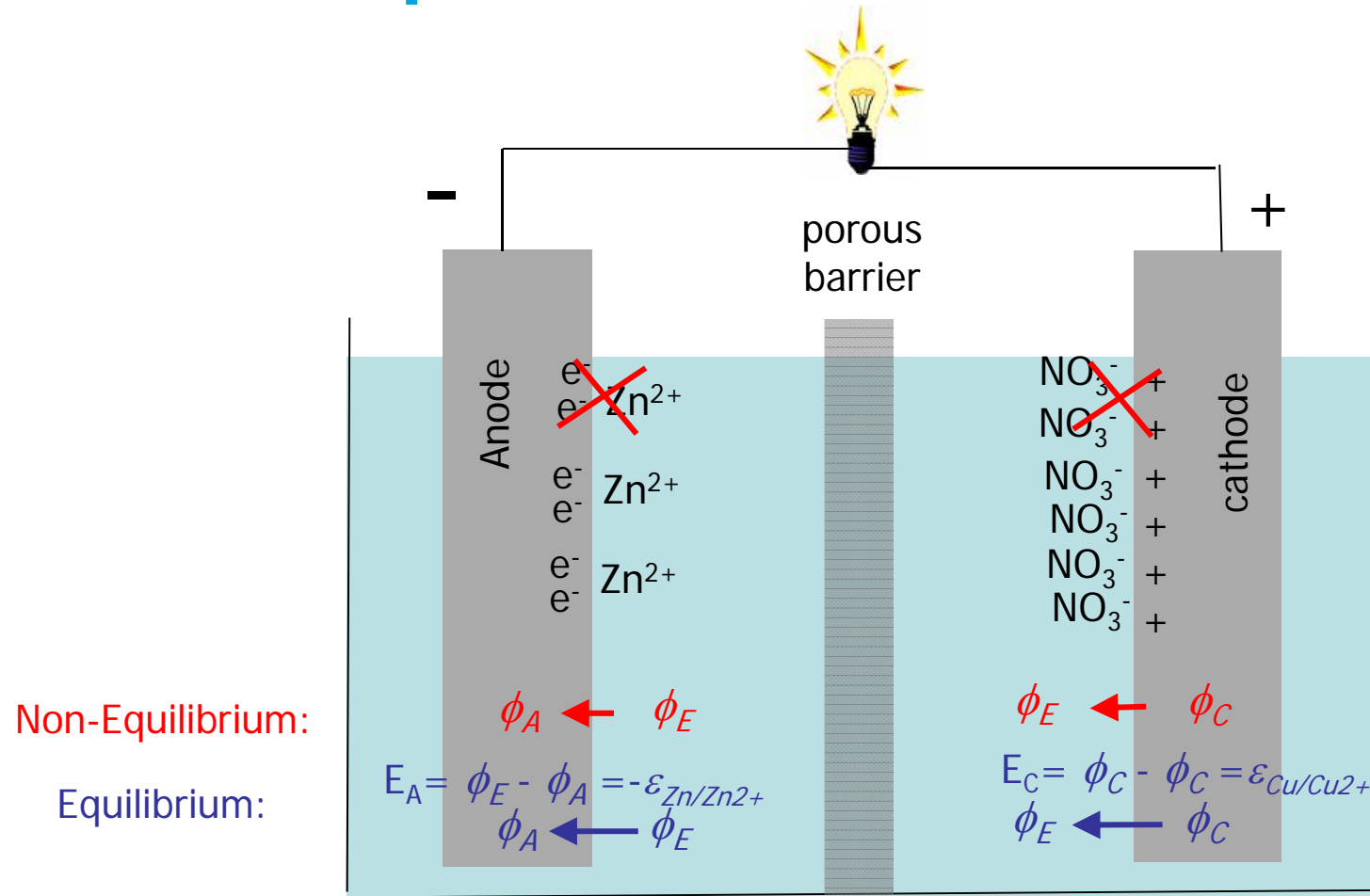
Change in equilibrium potential

Consequence of internal resistance: cell voltage will depend on current

Effect called: Polarization η

Galvanic cell (discharge): $E_{Discharge} < E_{Cell}$

Electrolytic (charge) : $E_{Charge} > E_{Cell}$
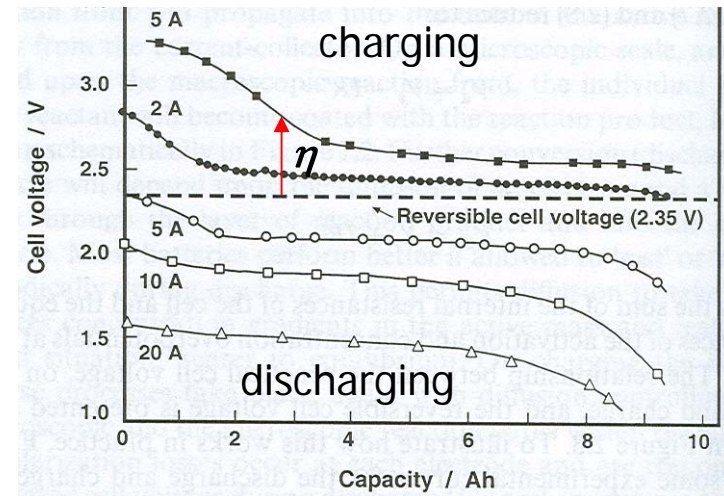
Also capacity (energy density) and therefore the efficiency depend on the (dis)charge rate!

$$Energy = \int E(Q)dQ \qquad Q: \text{Capacity (Coulomb)}$$

$$Efficiency = \frac{\int E_{Discharge}(Q)dQ}{\int E_{Charge}(Q)dQ}$$

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Change in equilibrium potential

$$Energy = \int E(Q)dQ \qquad Q\text{: Capacity (Coulomb)}$$
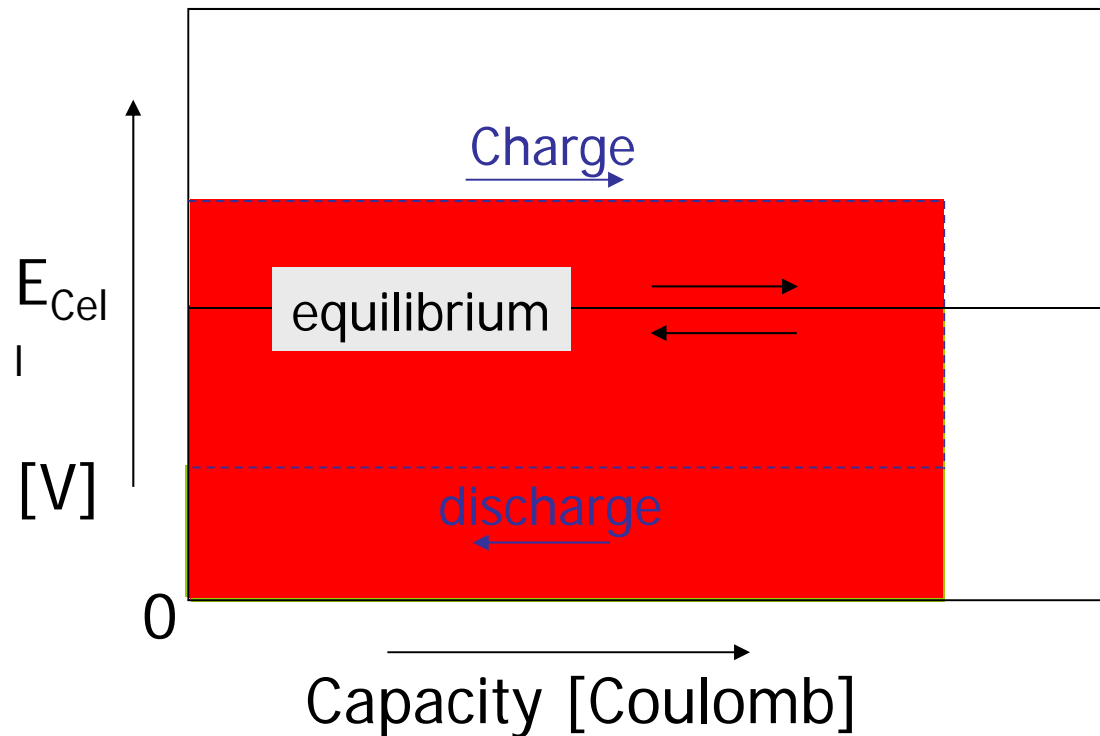
$$Efficiency = \frac{\int E_{\text{Discharge}}(Q)dQ}{\int E_{\text{Charge}}(Q)dQ}$$

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Different sources for the overpotential/internal resistance

$$\eta_{Total} = \eta_1 + \eta_2 + \eta_3 + \eta_4 \qquad r_{i,Total} = r_1 + r_2 + r_3 + r_4$$

(1) ionic conduction A^+ through the electrolyte
(2) Charge transport over the electrolyte-electrode interface
(3) solid state ionic conduction A or B
(4) electronic conduction

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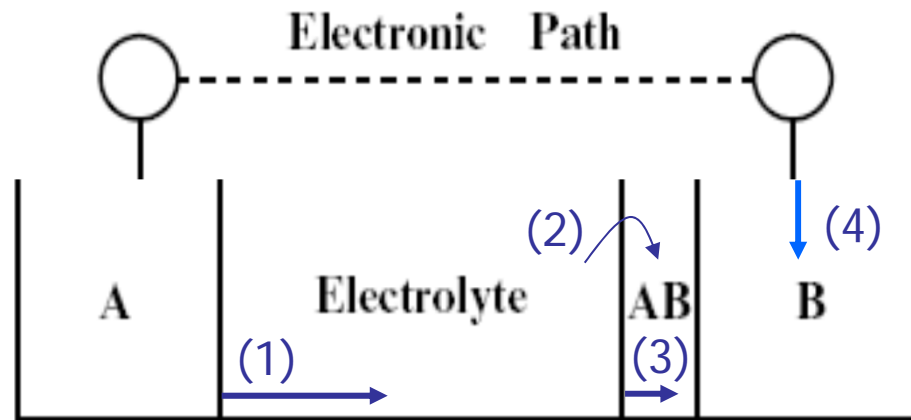
Ionic diffusion through the electrolyte

Example: Reduction: $Cu^{2+} + 2e^- \rightarrow Cu(s)$ (cathodic)

η_1: **resistance due to finite conductivity electron/ion in the electrode/electrolyte**

Diffusion of Cu^{2+} will be hindered by attracted molecules increasing its effective radius and thereby increasing its resistance.

Ohmic behaviour: $\eta_1 = Ir_{i,1}$

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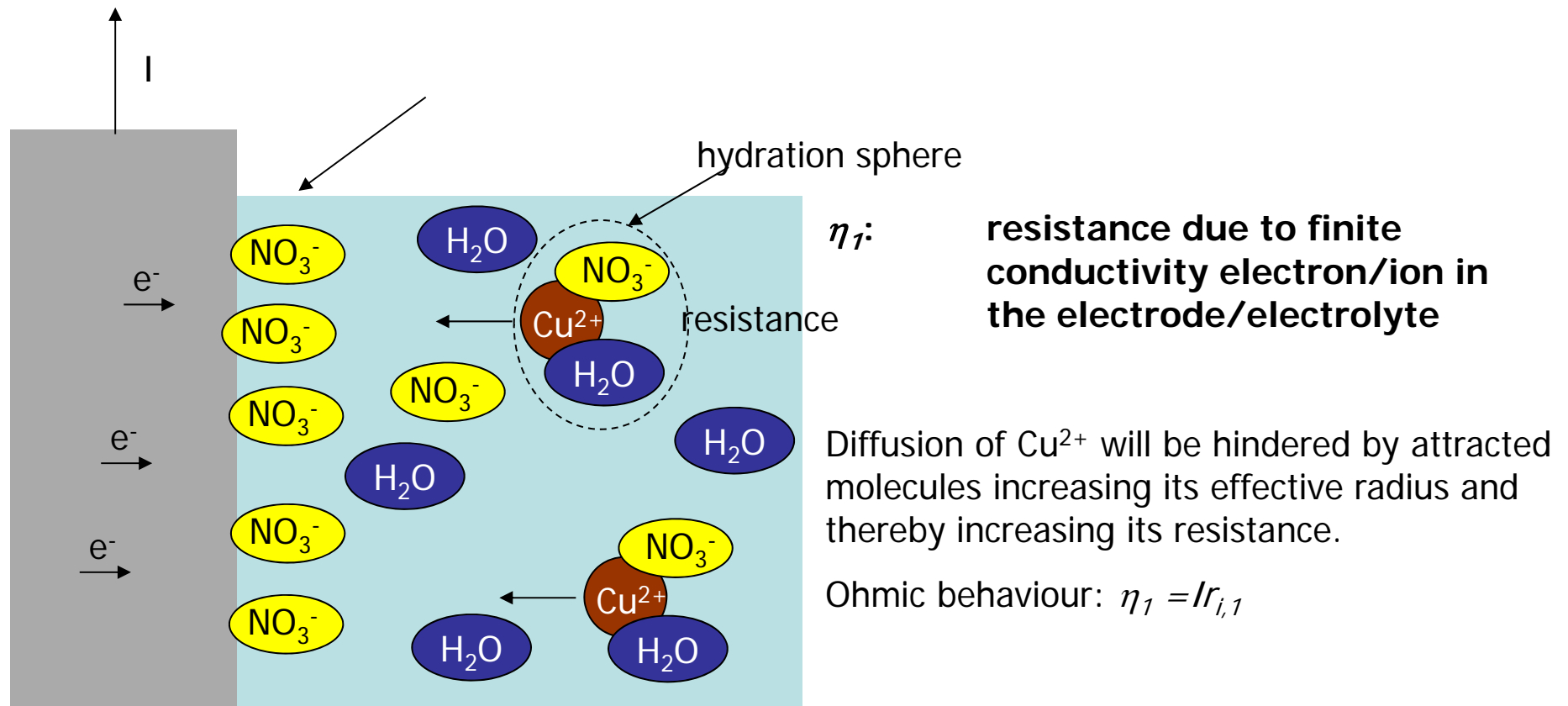
Ionic diffusion through the electrolyte

Mass transport through diffusion (related to overpotential η_1)

$$O + ze^- \rightarrow R$$
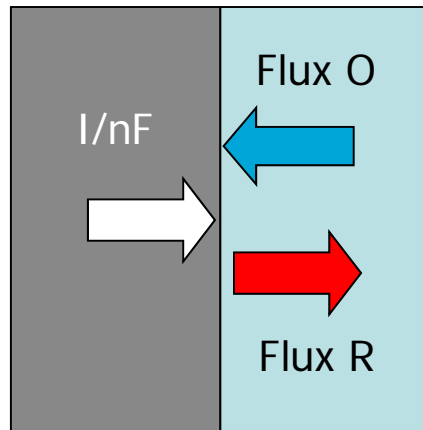
Ionic diffusion through the electrolyte:

Fick 1st law Flux (mol/s):

Flux O

I/nF

Flux R

$$J = -D \frac{dc}{dx}$$

$$\frac{I}{zF} = -D_{Ox} \frac{dc_{Ox}}{dx}$$

$$\frac{I}{zF} = -D_{Red} \frac{dc_{Red}}{dx}$$

Remember: $\mu = \mu^o + RT\, lnc$ -> concentration gradient -> mass flow

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Ionic diffusion through the electrolyte

Time dependent mass transport (derive Fick 2nd law)

Fick 1st law:

Distance to electrode: x   dx

$$Flux = -D\frac{dc_i(x)}{dx}$$

Flux in   Flux out
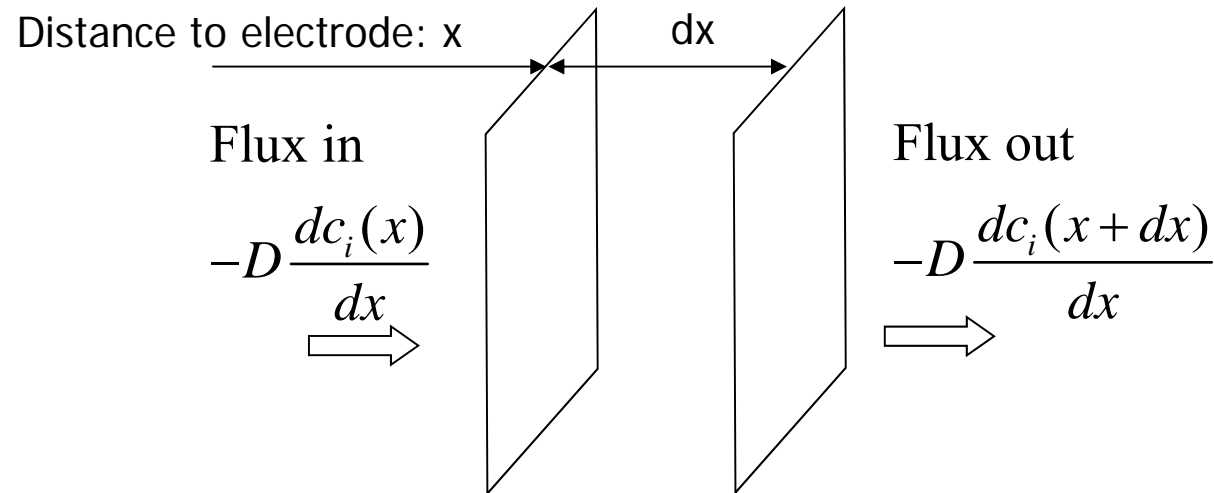
$$-D\frac{dc_i(x)}{dx}$$ $$-D\frac{dc_i(x+dx)}{dx}$$

Change in time *dt* of *c$_i$(x)* equals the difference in Flux in and out:

$$\frac{dc_i(x)}{dt} = -D\left[\frac{dc_i(x)}{dx} - \frac{dc_i(x+dx)}{dx}\right] = D\frac{d^2c_i(x)}{dx^2}$$ *: Fick 2nd law*

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Ionic diffusion through the electrolyte

$$I = -zFD \frac{dc_i(x)}{dx}$$

$$\frac{dc_i(x)}{dt} = D \frac{d^2 c_i(x)}{dx^2}$$

To be able to calculate the current, I, that the electrolyte can pass:

(1) We need *c(x)*:   solution of differential equation, depends on conditions
(2) We need *D:*   Measured property (how to measure?)

Ionic diffusion through the electrolyte

O + ne$^-$ → R (reduction)
O + ne$^-$ <- R (oxidation)
(Cu^{2+} + 2e$^-$ <-> Cu)
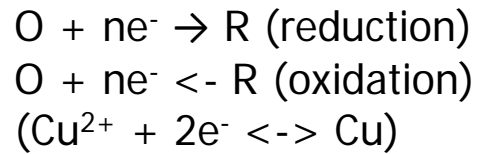
Experiment: $t=0$ $\varepsilon_{App} = \varepsilon_{eq}$

  t>0 $\varepsilon_{App} < \varepsilon_{eq}$

Starting concentration O: c_O^{inf}
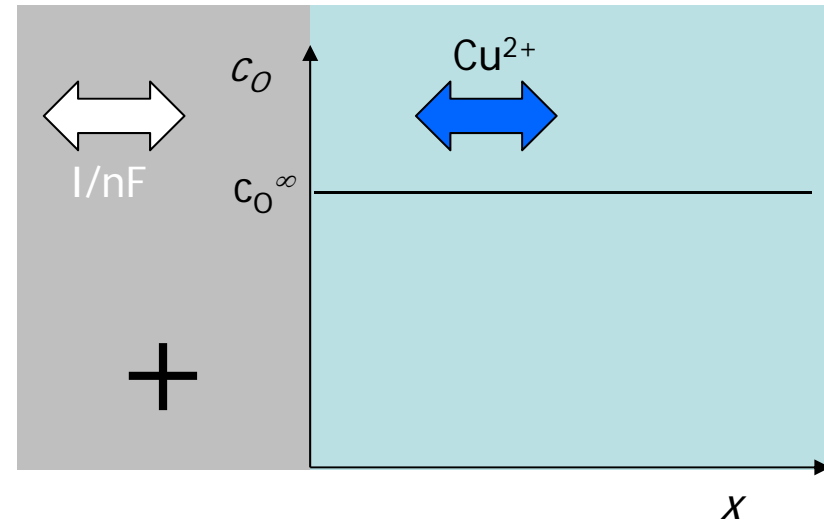
Questions: (1) How does the current look as a function of time?
(2) How to determine the diffusion coefficient

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Question kinetics 3

Suppose we impose $\varepsilon_{App} < \varepsilon_{Eq}$ what will happen?
a) netto reduction
b) netto oxidation
c) nothing
d) no clue

$Cu^{2+} + 2e^- \rightarrow Cu$ (reduction)
$Cu^{2+} + 2e^- \leftarrow Cu$ (oxidation)

$$\varepsilon_{eq} = \varepsilon^0 - \frac{RT}{zF} \ln\left(\frac{c_{Cu}}{c_{Cu^{2+}}} \right)$$

$$\varepsilon_{App} < \varepsilon_{eq} = \varepsilon^0 - \frac{RT}{zF} \ln\left(\frac{c_{Cu}}{c_{Cu^{2+}}} \right)$$

$$\Rightarrow c_{Cu} > c_{Cu^{2+}} \quad Cu^{2+} \text{ is converted to Cu}$$

$$\Rightarrow \text{ netto reduction (cathodic current)}$$

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Ionic diffusion through the electrolyte

O + ne⁻ -> R (reduction)

Experiment: $t=0$ $\varepsilon_{App} = \varepsilon_{eq}$

$t>0$ $\varepsilon_{App} < \varepsilon_{eq}$

Starting concentration O: c_O^{inf}
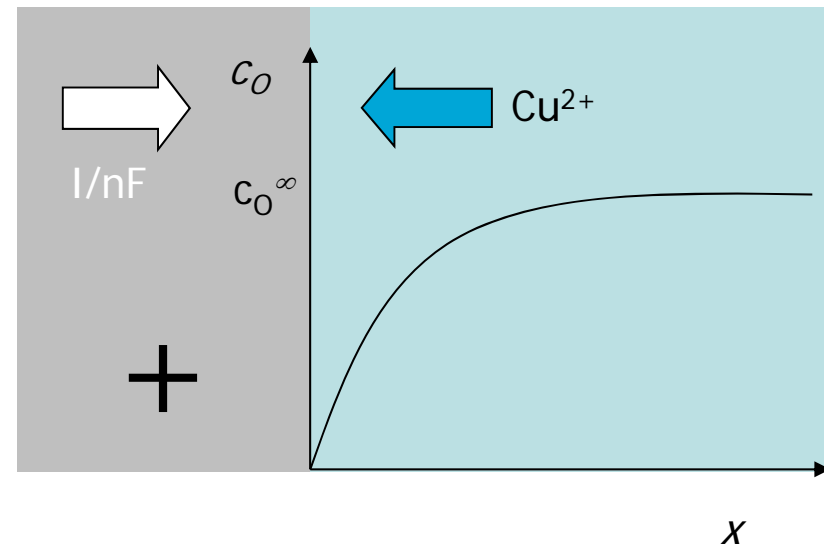
Question: (1) How does the current look as a function of time?

Solve $c(x)$ from: $$\frac{dc_i(x)}{dt} = D\frac{d^2c_i(x)}{dx^2}$$ $\Longrightarrow$ $$I = -zFD\frac{dc_i(x)}{dx}$$
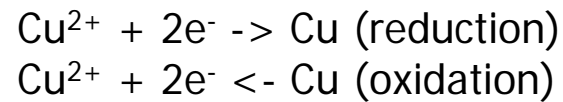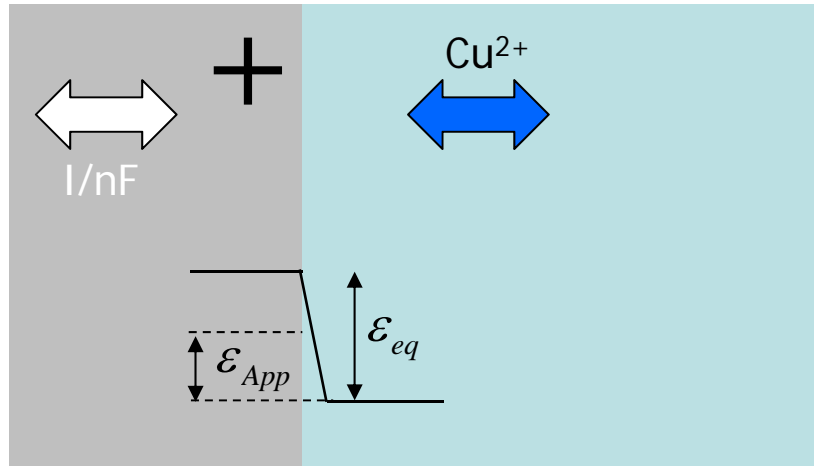
Ionic diffusion through the electrolyte

O + ne⁻ -> R (reduction)

Experiment: $t=0$ $\varepsilon_{App} = \varepsilon_{eq}$

                 $t>0$ $\varepsilon_{App} < \varepsilon_{eq}$

Starting concentration O: c_O^{∞}

$\Rightarrow$ Boundary/initial conditions for $\dfrac{dc_i(x)}{dt} = D\dfrac{d^2 c_i(x)}{dx^2}$

Initial condition t=0: $c_O(t=0, x) = c_O^{\infty}$

Boundary condition $x=0$ $c_O(t, x=0) = 0$ ⟵   Charge transfer is not rate limiting
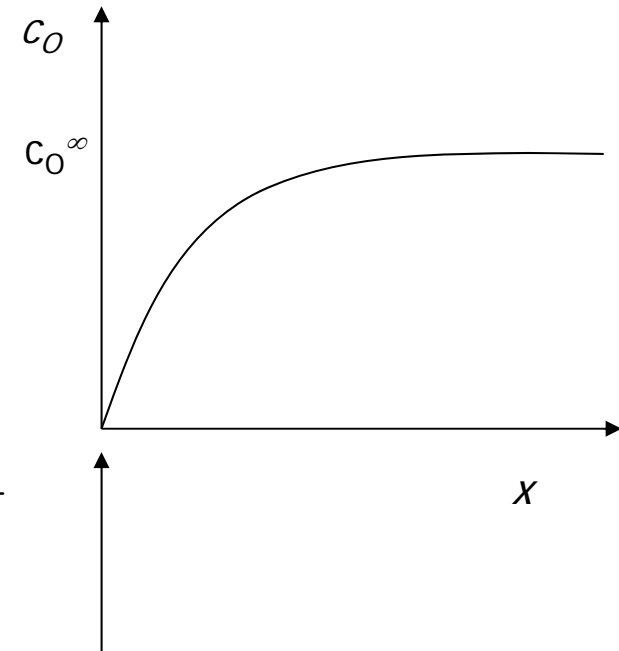
                    $x=\infty$ $c_O(t, x=\infty) = c_O^{\infty}$

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Ionic diffusion through the electrolyte

Solutions of $\dfrac{dc_i(x)}{dt} = D\dfrac{d^2 c_i(x)}{dx^2}$ usually have the form of an error function

$$erf(x) = \frac{2}{\pi^{1/2}} \int_0^x \exp(-t^2)\,dt$$

It appears (can be derived via Laplace):

$$c_0(t,x) = c_0^{\infty}\, erf\left(\frac{x}{\sqrt{4Dt}}\right)$$

Oxidant concentration after potential step
$c_O(t=0) = 1$ mol/l

$\sqrt{4Dt}$

Legend:
- t=0.0 s
- t=0.1 s
- t=0.5 s
- t=1.0 s
- t=2.0 s
- t=6.0 s

y-axis: c_O [mol/l]
x-axis: distance perpendicular electrode interface (μm)

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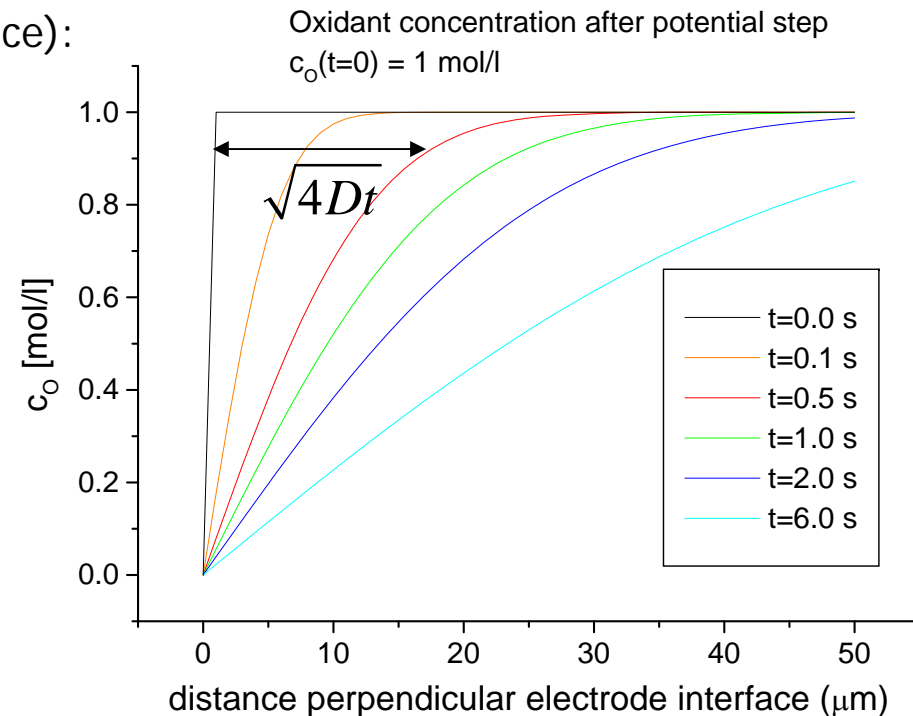
Ionic diffusion through the electrolyte

$$\frac{I}{zF} = -D_O \left[\frac{dc_O(t,x)}{dx} \right]_{x=0}$$

$$I = -zFD_O \frac{c_O^\infty}{\sqrt{\pi D_O t}} \exp\left(\frac{-x^2}{4D_O t} \right)$$

$$I(x=0) = -zFc_O^\infty \sqrt{\frac{D_O}{\pi t}}$$

$$erf(x) = \frac{2}{\pi^{1/2}} \int_0^x \exp(-t^2)dt$$

$$\frac{derf(x)}{dx} = \frac{2}{\pi^{1/2}} \exp(-x^2)$$

The current as a function of time after the potential step $\varepsilon_{App} < \varepsilon_{eq}$

Current density after potential step
$c_O = 1$ mol/l

Legend:
- D=1.0 10^{-6} cm^2/s
- D=2.0 10^{-6} cm^2/s
- D=0.5 10^{-6} cm^2/s

Y-axis: Current density I (A/cm^2)
X-axis: time [s]

Measurement of current after potential step leads to diffusion coefficient!

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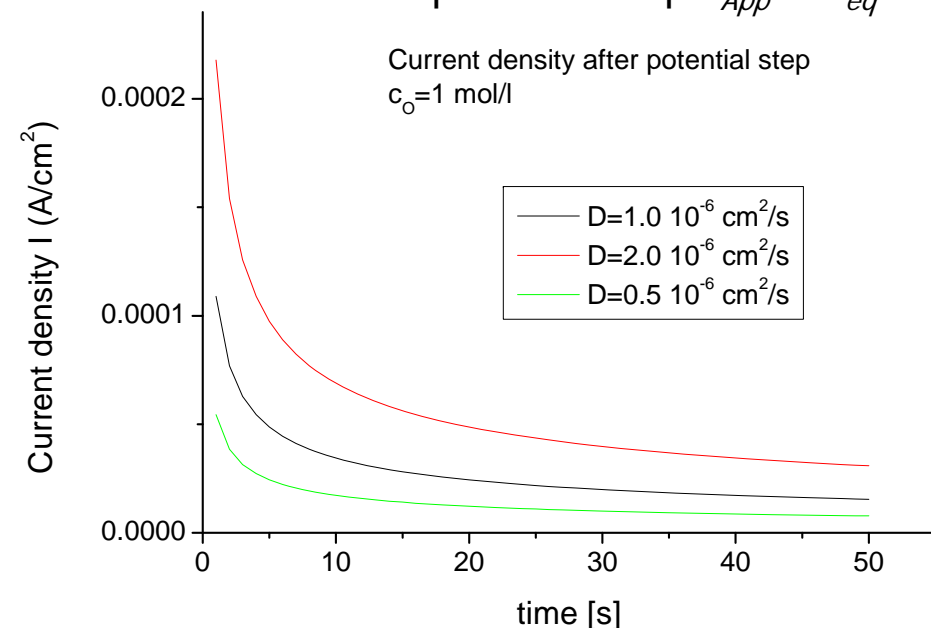
Ionic diffusion through the electrolyte

$$\frac{I}{zF} = -D_O \left[\frac{dc_O(t,x)}{dx} \right]_{x=0}$$

Higher concentrations -> larger gradients -> higher currents?

Dependence D on Temperature
and concentration LiPF$_6$ salt:
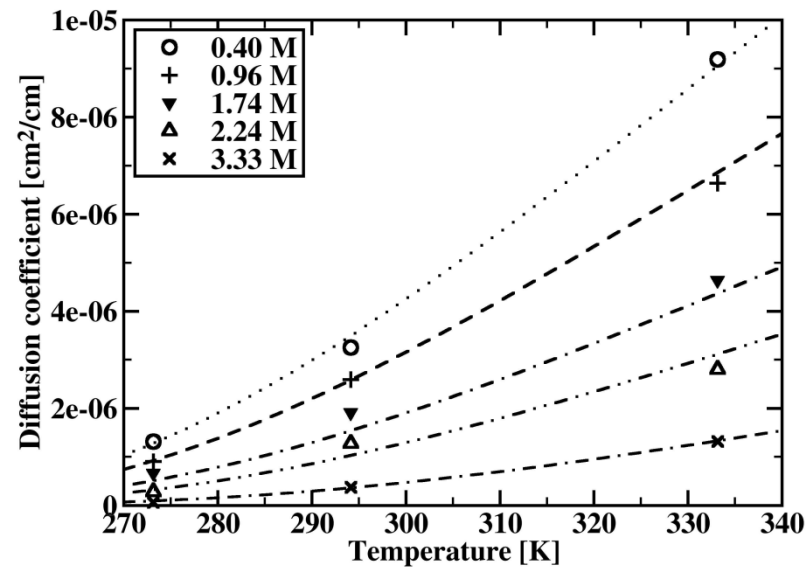
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Different sources for the overpotential/internal resistance

$$\eta_{Total} = \eta_1 + \eta_2 + \eta_3 + \eta_4 \qquad r_{i,Total} = r_1 + r_2 + r_3 + r_4$$

(1) ionic conduction A^+ through the electrolyte
(2) Charge transport over the electrolyte-electrode interface
(3) solid state ionic conduction A or B
(4) electronic conduction

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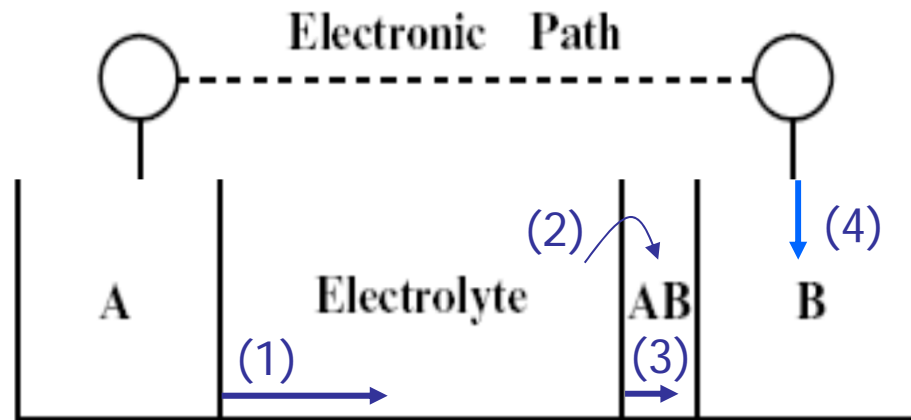
What do we want?

Predict current given the overpotential: $I(\eta)$
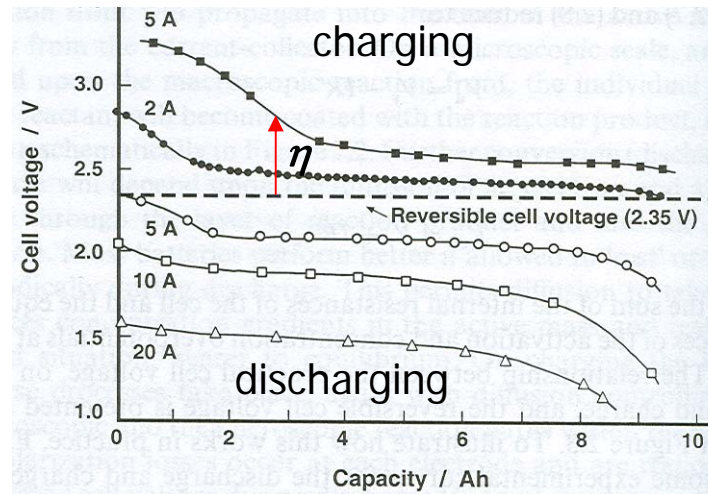
Kinetic electrochemistry, charge transfer
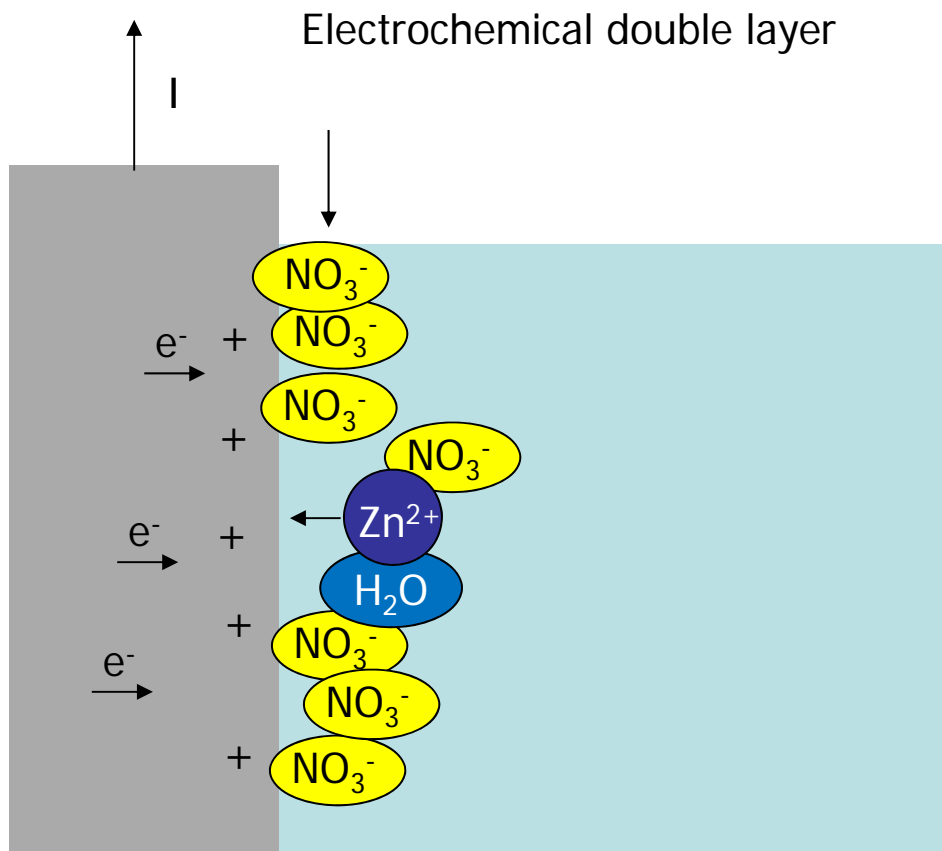
Example: Reduction: $Zn^{2+} + 2e^- \rightarrow Zn(s)$ (cathodic)

Electrochemical double layer

I

e⁻ +

NO₃⁻
NO₃⁻
NO₃⁻
NO₃⁻

e⁻ +

Zn²⁺

H₂O

e⁻ +

NO₃⁻
NO₃⁻
NO₃⁻

Step 1: **enter the electrical double layer and loose hydration sphere**

Step 2: electron transfer

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Kinetic electrochemistry, charge transfer

Example: Reduction: $Zn^{2+} + 2e^- \rightarrow Zn(s)$ (cathodic)

I

E_{Fermi}

e^- e^- e^- e^-

e^- e^- LUMO

Cu^{2+}
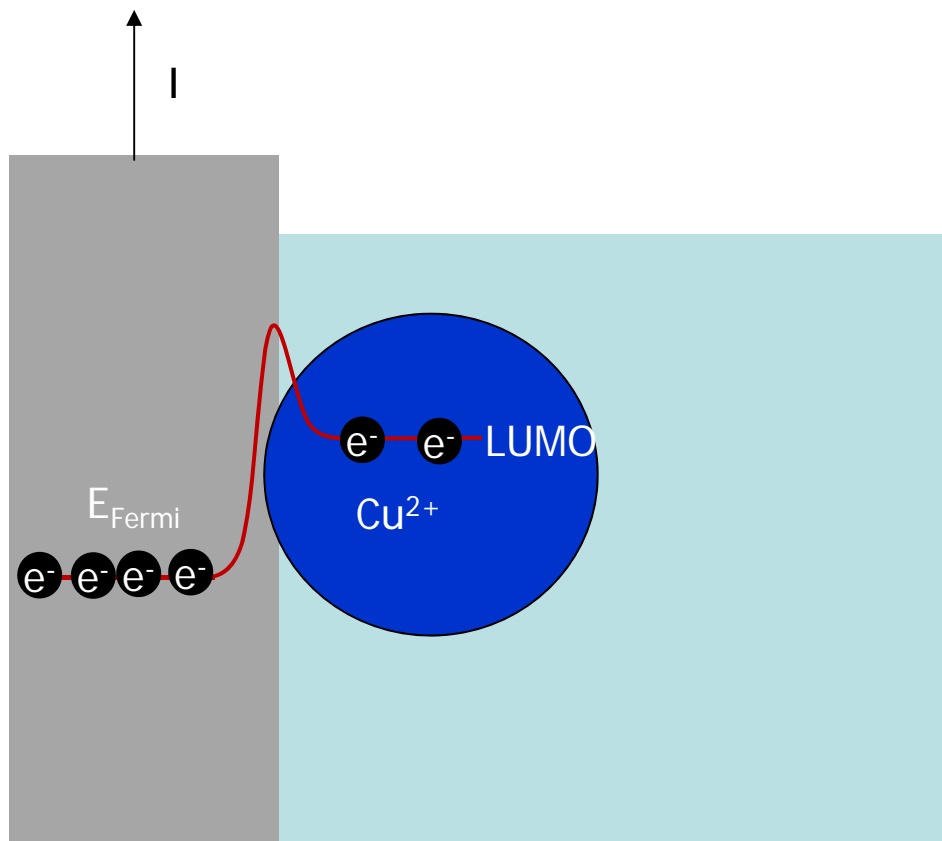
Step 1: enter the electrical double layer and loose hydration sphere

Step 2: electron transfer

LUMO: Lowest unoccupied molecular orbital

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Although during discharge the charge transfer process is spontaneous, it does need to overcome a barrier (step 1 and 2).
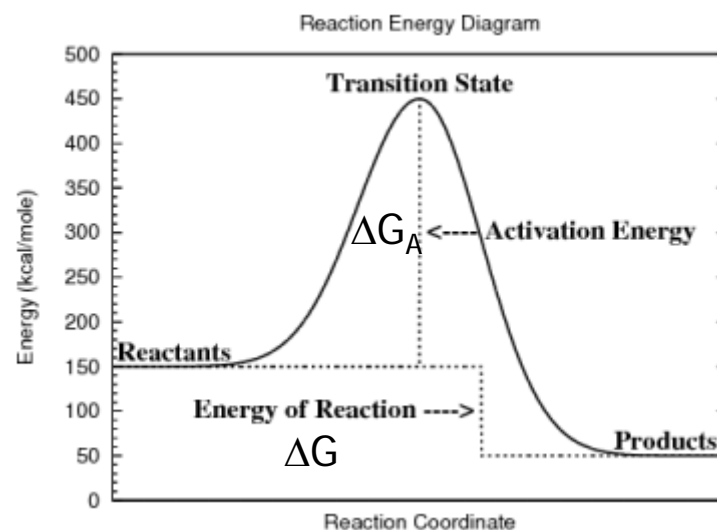
Relationship of the current density [A/cm^2] with the activation barrier ΔG_A, Arrhenius law:

$$i = zFcke^{-\frac{\Delta G_A}{RT}}$$

c: concentration [mol/cm^3], F: Faradays constant [C/mol] and k: rate constant [cm/s]

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Outer Helmolz Plane

e⁻ e⁻ e⁻ e⁻

M

Electrochemical Double Layer (EDL)

M^{z+} M^{z+} M^{z+} M^{z+}

Reduction: $M \leftarrow M^{+z} + ze^-$ (cathodic)

Oxidation: $M \rightarrow M^{+z} + ze^-$ (anodic)

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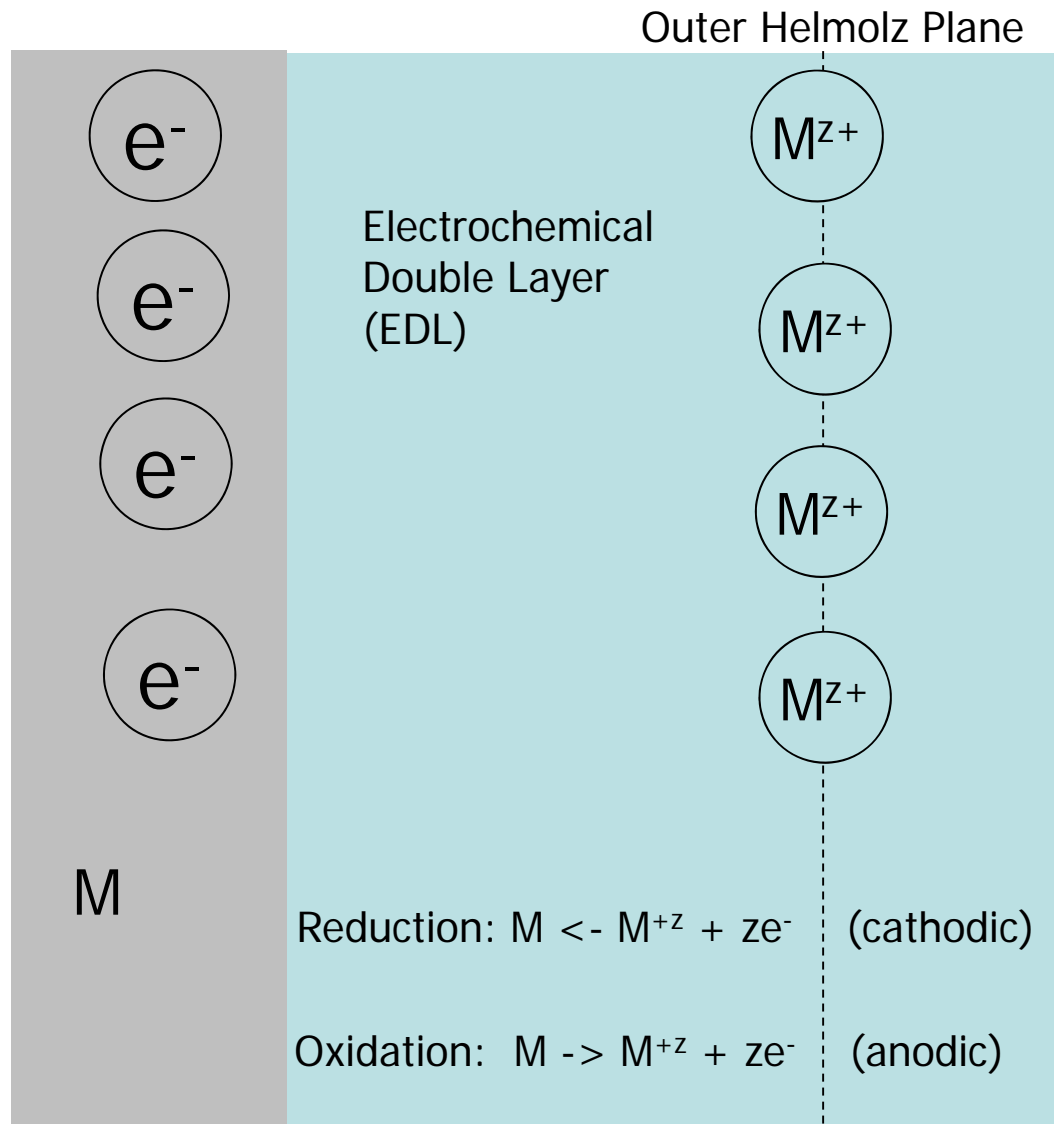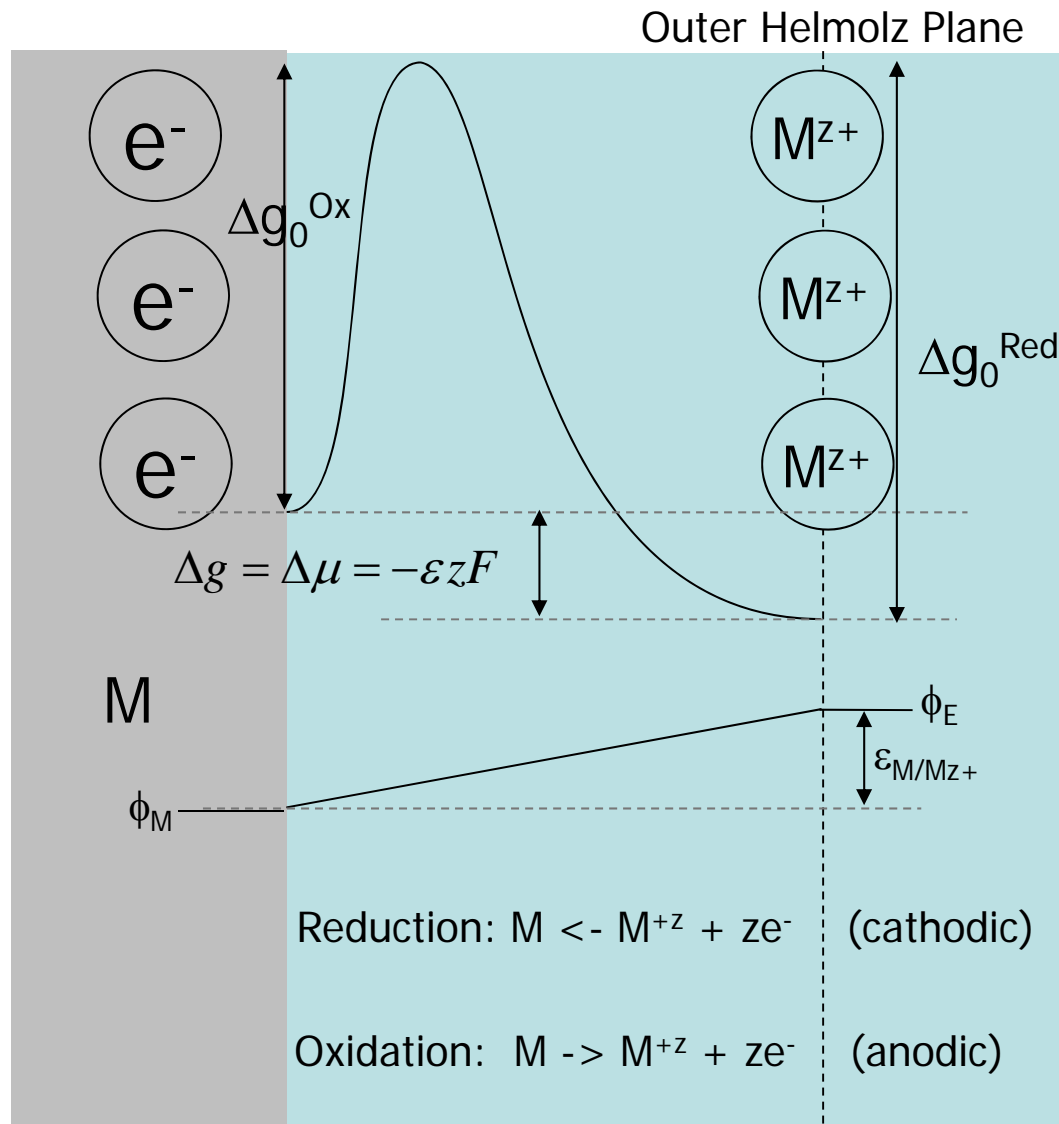
Difference in chemical potenital is difference in Gibbs free energy per mol

$$dG = Vdp - SdT + \sum_j \mu_j dn_j \overset{\text{Constant p and T}}{=} \sum_j \mu_j dn_j = -EdQ$$

$$dG = \sum_j \mu_j dn_j = -\varepsilon_{M/Mz+} dQ$$

Integrate over n moles

$$\Delta G = \left(\mu_{M^{z+}} - \mu_M\right)n = -\varepsilon_{M/Mz+}\Delta Q$$

$$\Delta G = \left(\mu_{M^{z+}} - \mu_M\right)n = -\varepsilon_{M/Mz+}znF$$

$$\Delta g = \left(\mu_{M^{z+}} - \mu_M\right) = -\varepsilon_{M/Mz+}zF$$

$$\Delta g = \Delta\mu = -\varepsilon zF$$

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OHP

$\Delta g_0{}^{Ox}$

$\Delta g_0{}^{Red}$

$\Delta g = \Delta \mu = -\varepsilon z F$

ϕ_E

$\varepsilon_{M/Mz+}$

ϕ_A

Reduction: M <- M^{+z} + ze$^-$ (cathodic)
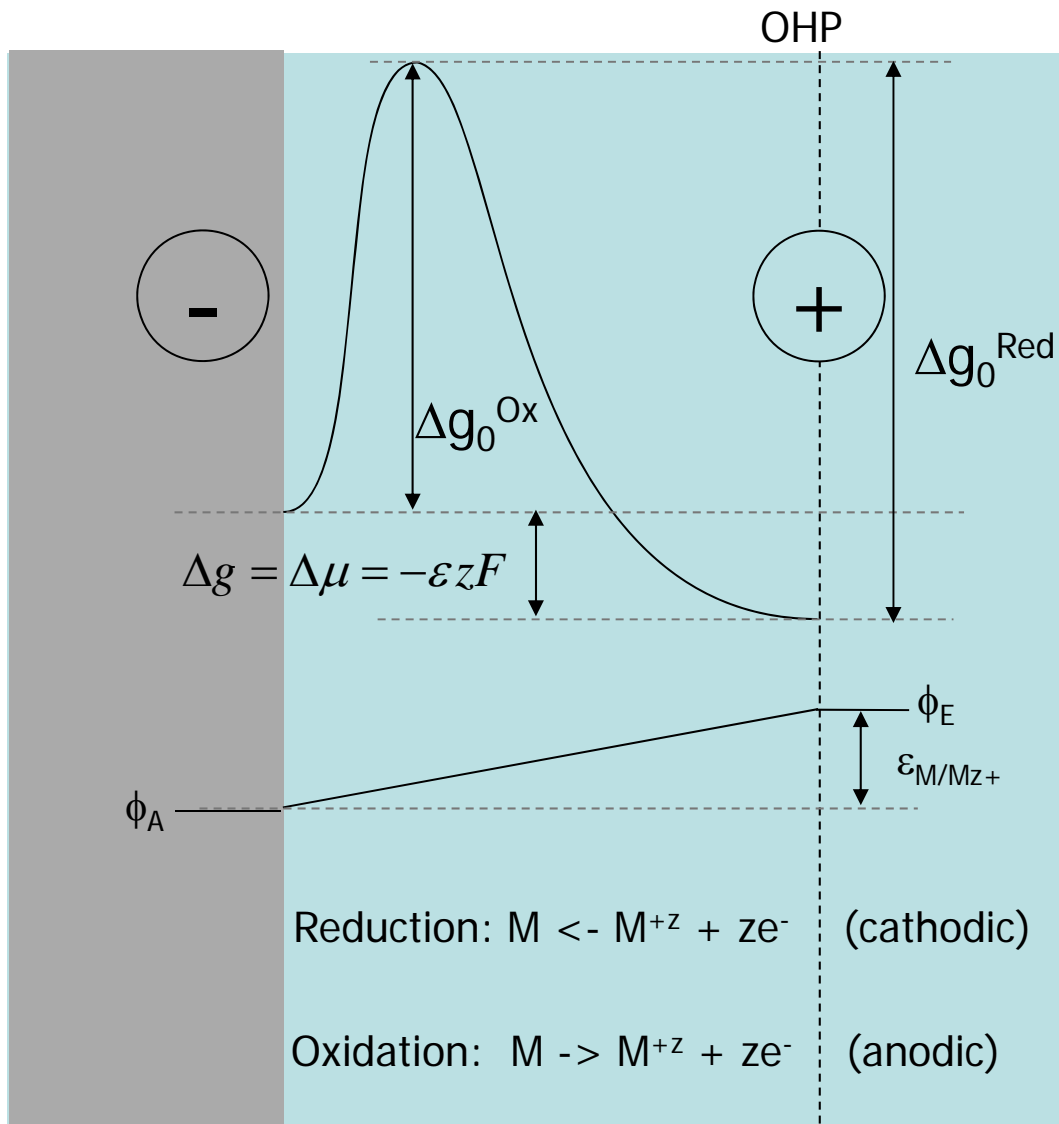
Oxidation: M -> M^{+z} + ze$^-$ (anodic)

Situation:

Equilibrium has established at open circuit. The difference in chemical potential is compensated by the field.

Both reduction and oxidation occur, in the same rate!

Dynamic equilibrium:

Zero netto current: $i_{netto} = i_A - i_C = 0$ definition exchange current density (equilibrium current): $i_0 = i_A = i_C$

$$i_0 = i_C = zFc_O k_C e^{-\frac{\Delta g_0{}^{Red}}{RT}}$$

$$i_0 = i_A = zFc_R k_A e^{-\frac{\Delta g_0{}^{Ox}}{RT}}$$

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Question Kinetics 4
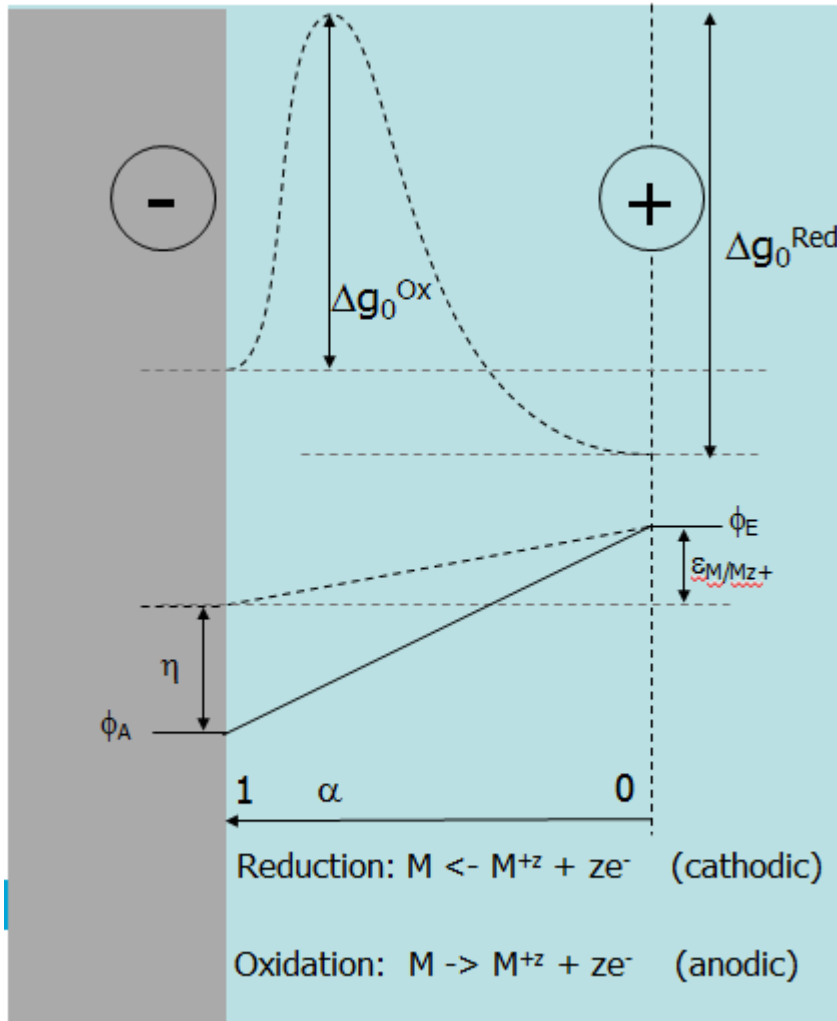
What will happen with the barrier for reduction, Δg_0^{Red}, if the over- potential η will be applied?

a) Δg_0^{Red} increases

b) Δg_0^{Red} decreases

c) Δg_0^{Red} remains the same

d) No clue

What will be the result?

a) Effective oxidation

b) Effective reduction

c) Nothing

d) No clue

What will happen with the barrier for reduction, Δg_0^{Red}, if the over- potential η will be applied?

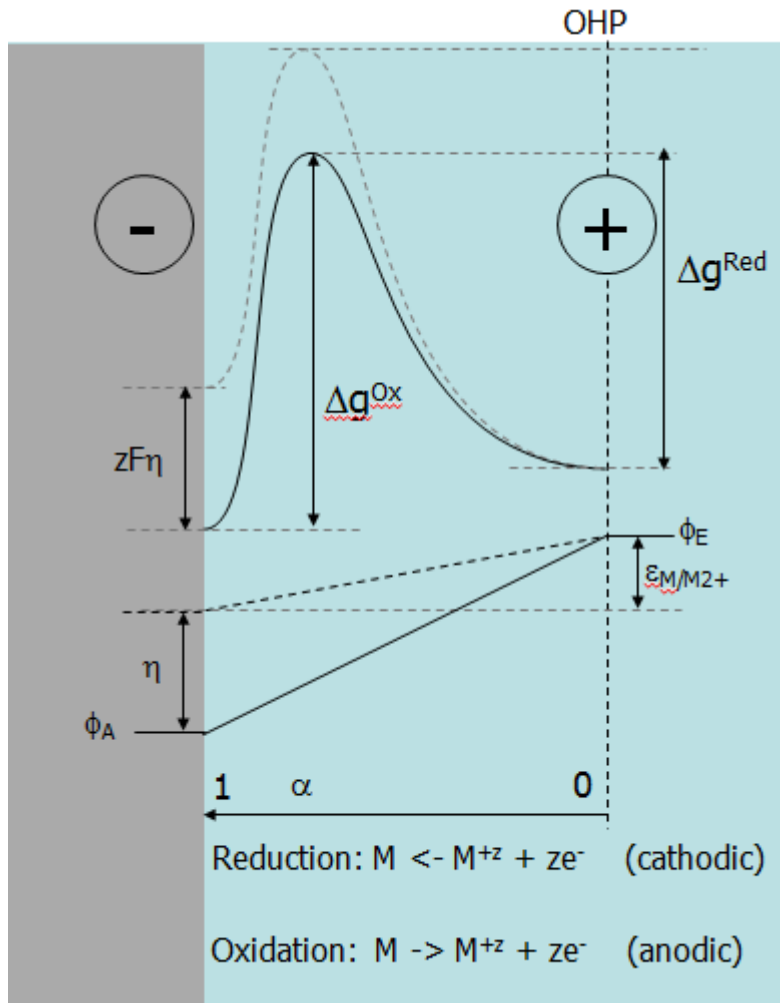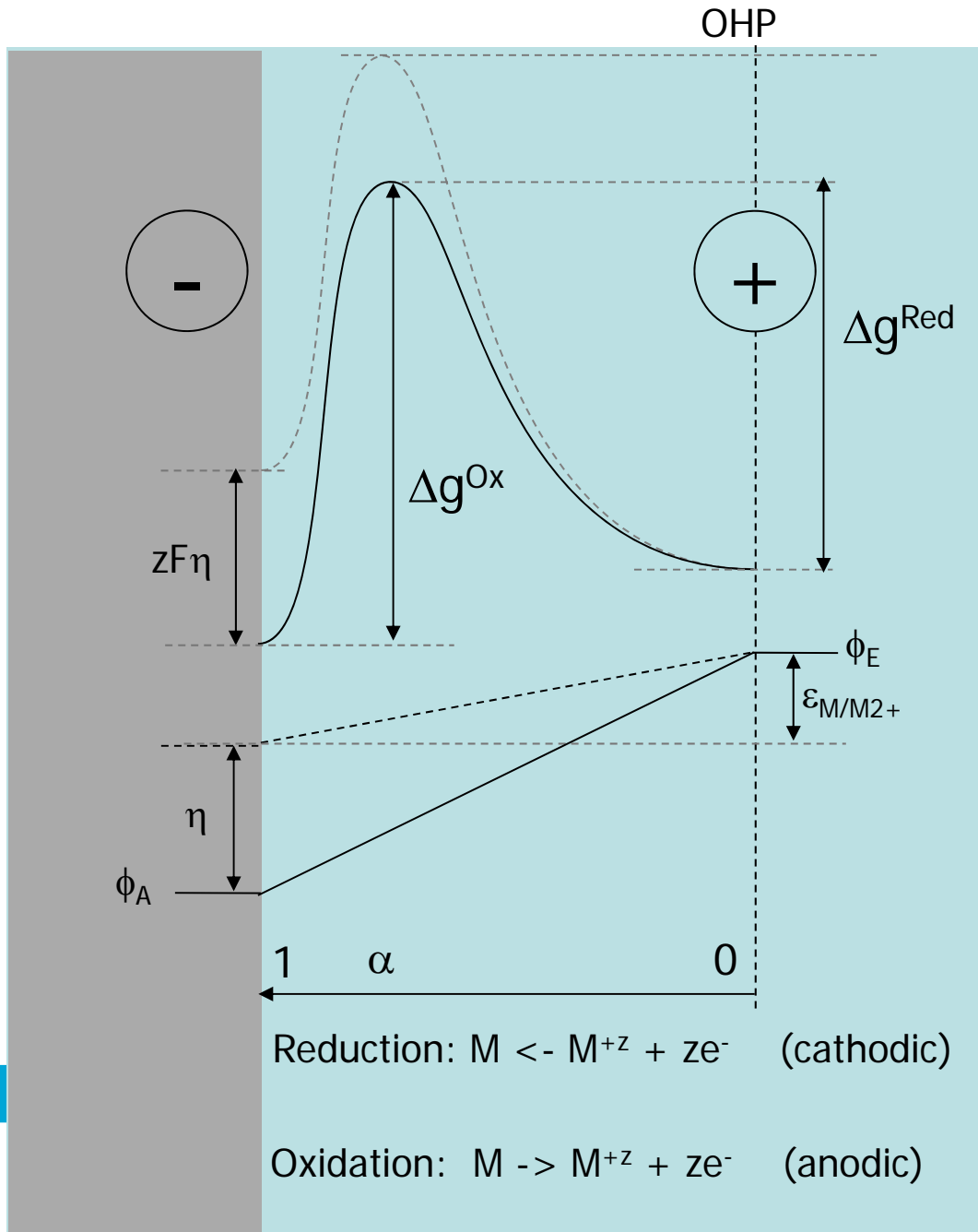a) Δg_0^{Red} increases

b) Δg_0^{Red} decreases

c) Δg_0^{Red} remains the same

d) No clue

What will be the result?

a) Effective oxidation

b) Effective reduction

c) Nothing

d) No clue

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OHP

−

+

Δg^{Red}

Δg^{Ox}

zFη

ϕ_E

$\epsilon_{M/M2+}$

η

ϕ_A

1   α   0

Reduction: M <- M⁺ᶻ + ze⁻   (cathodic)

Oxidation: M -> M⁺ᶻ + ze⁻   (anodic)

Situation:

Polarized state, pumping electrons in the negative electrode (charging), Δg^{red} : effectively reduction: $i_C > i_A$

The new barriers will be:

$$\Delta g^{Ox} = \Delta g_0^{Ox} + (1-\alpha)zF\eta$$
$$\Delta g^{Red} = \Delta g_0^{Red} - \alpha zF\eta$$

$$i_C = zFc_O k_C e^{-\frac{\Delta g^{Red}}{RT}}$$

$$i_A = zFc_R k_A e^{-\frac{\Delta g^{Ox}}{RT}}$$

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Kinetic electrochemistry, charge transfer

Fill in the barriers upon polarization:

$$i_C = zFc_Ok_Ce^{-\frac{\Delta g^{Red}}{RT}} = zFc_Ok_Ce^{-\frac{\Delta g_0^{Red}}{RT}}e^{-\frac{\alpha zF\eta}{RT}} = i_0e^{-\frac{\alpha zF\eta}{RT}}$$

$$i_A = zFc_Rk_Ae^{-\frac{\Delta g^{Ox}}{RT}} = zFc_Rk_Ae^{-\frac{\Delta g_0^{Ox}}{RT}}e^{\frac{(1-\alpha)zF\eta}{RT}} = i_0e^{\frac{(1-\alpha)zF\eta}{RT}}$$

In equilibrium, $\eta=0$, $i_C=i_A=i_0$ => $i_{Netoo}= i_A - i_C = 0$
in that condition we define $i_C=i_A=i_0$ as the exchange current density

$$i_0 = i_A = i_C = zFc_Ok_Ce^{\frac{-\Delta g_0^{Red}}{RT}} = zFc_Rk_Ae^{\frac{-\Delta g_0^{Ox}}{RT}}$$

What is so important about the exchange current density i_0?

Quantitative measure of the amount of electron transfer activity at equilibrium

i_o large $\Rightarrow$ much simultaneous ox/red electron transfer (ET) $\Rightarrow$ inherently fast ET (kinetics)
i_o small $\Rightarrow$ little simultaneous ox/red electron transfer (ET) $\Rightarrow$ sluggish ET reaction (kinetics)

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Kinetic electrochemistry, charge transfer

So for the netto current density (difference anodic and cathodic current at one electrode):

$$i_{netto} = i(\eta) = i_A - i_C = i_0 \left(e^{\frac{(1-\alpha)zF\eta}{RT}} - e^{-\frac{\alpha zF\eta}{RT}} \right) \quad \text{Butler-Volmer equation}$$

This is the fundamental equation of electrode kinetics, relates the **current density** with the exchange current density, the **overpotential** η and the transfer coefficient.

Remember, we only considered the charge transfer at the electrode-electrolyte interface (η_2)

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Kinetic electrochemistry, charge transfer

In practice the two following limiting cases of the Butler-Volmer equations are most important:

(1) low overpotentials, $|\eta| = |\varepsilon_{Cell} - \varepsilon_{eq}| < 10$ mV

(2) high overpotentials, $|\eta| = |\varepsilon_{Cell} - \varepsilon_{eq}| > 50$ mV

$$i(\eta) = i_0 \left(e^{\frac{(1-\alpha)zF\eta}{RT}} - e^{-\frac{\alpha zF\eta}{RT}} \right)$$

Case 1: Low Overpotential

Here we can use a Taylor expansion to represent e^x:

$$e^x = 1 + x + \ldots$$

Ignoring higher order terms:

$$i = i_0 \left(1 + \frac{(1-\alpha)zF\eta}{RT} - \left(1 - \frac{\alpha zF\eta}{RT} \right) \right) = i_0 \frac{\alpha zF\eta}{RT}$$

so total current density varies linearly with the overpotential η near ε_{eq}

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Kinetic electrochemistry, charge transfer

$$i(\eta) = i_A - i_C = i_0 \left(e^{\frac{(1-\alpha)zF\eta}{RT}} - e^{-\frac{\alpha zF\eta}{RT}} \right)$$

Case 2: High Overpotential

what happens as η becomes a large negative value?   => $i_C >> i_A$

We can neglect i_A term as rate of oxidation becomes negligible:

$$i = i_C = i_0 e^{-\frac{\alpha zF\eta}{RT}}$$

So, current density varies exponentially with η, or taking the *ln* on both sides:
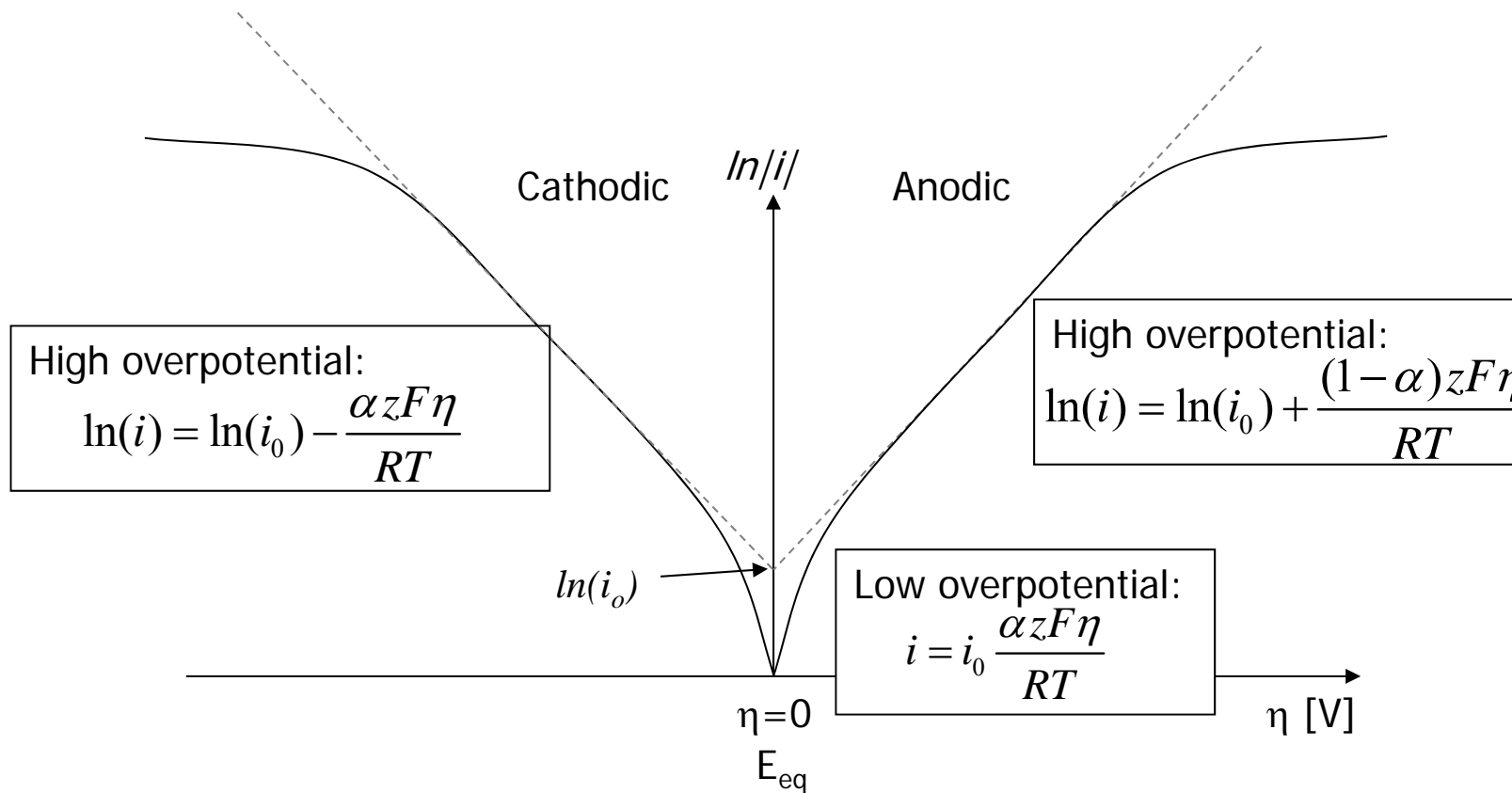
$$\ln(i) = \ln(i_0) - \frac{\alpha zF\eta}{RT}$$

This is the cathodic Tafel equation

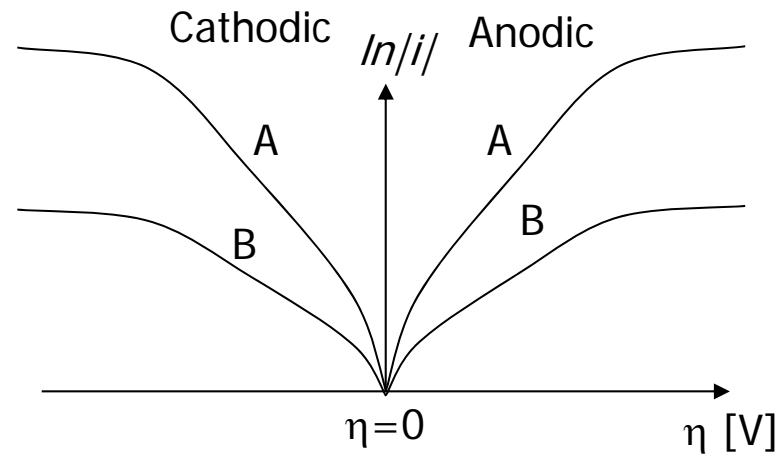Similar, if η becomes a large negative value ($i_A >> i_C$) we find the anodic Tafel equation:

$$\ln(i) = \ln(i_0) + \frac{(1-\alpha)zF\eta}{RT}$$

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Kinetic electrochemistry, charge transfer

Tafel Plots: Determine the exchange current density i_0 and the transfer coefficient α

Cathodic $\quad ln|i| \quad$ Anodic

High overpotential:
$$\ln(i) = \ln(i_0) - \frac{\alpha z F \eta}{RT}$$

High overpotential:
$$\ln(i) = \ln(i_0) + \frac{(1-\alpha) z F \eta}{RT}$$

$ln(i_o)$

Low overpotential:
$$i = i_0 \frac{\alpha z F \eta}{RT}$$
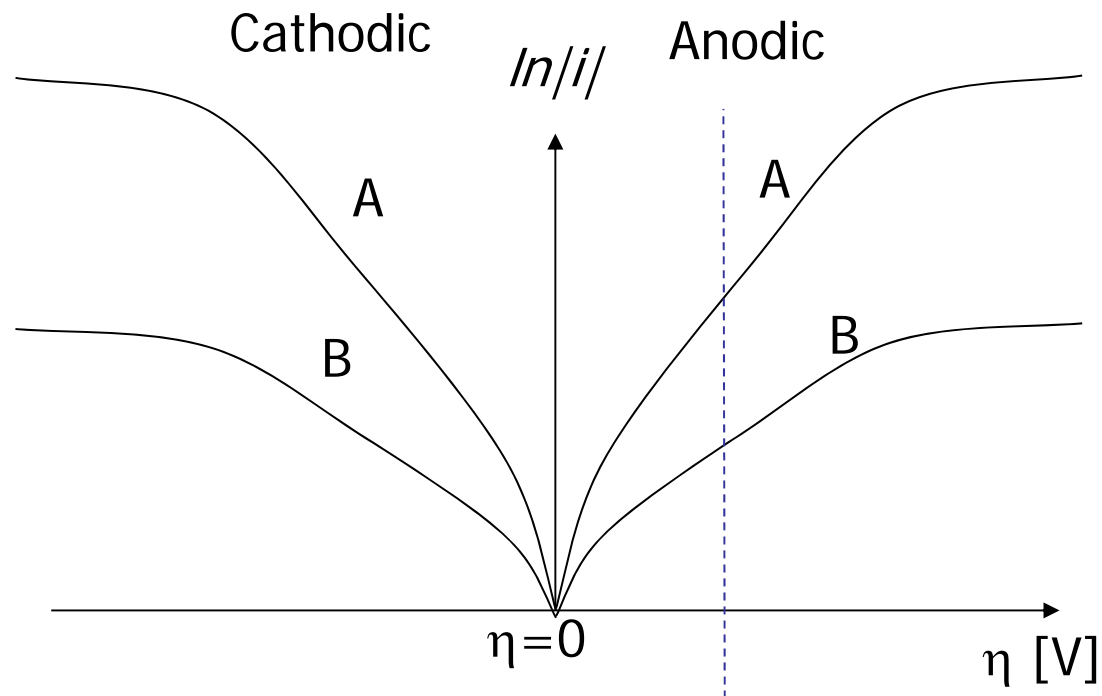
$\eta = 0$

E_{eq}

η [V]

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Question kinetics 5

Which curve represents the most sluggish reacting electrode?
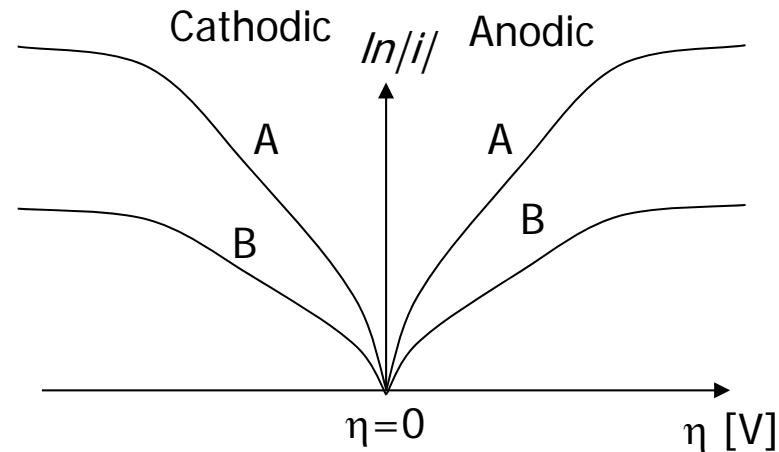
a) A

b) B

c) No clue

Question kinetics 5

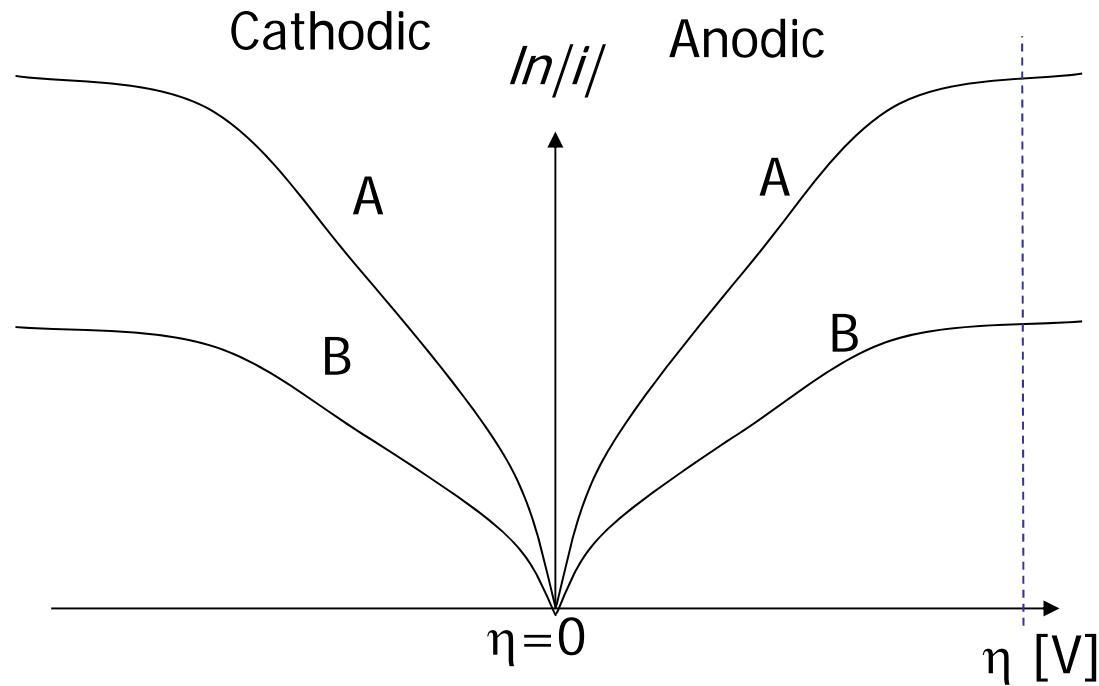A: higher current at the same overpotential => a) curve A more sluggish

Question kinetics 6

Why do the curves deviate from the Buttler Volmer relation at high overpotential?

a) Buttler-Volmer is not valid

b) No reacting species can be delivered due to the high rate

c) Because of side reactions
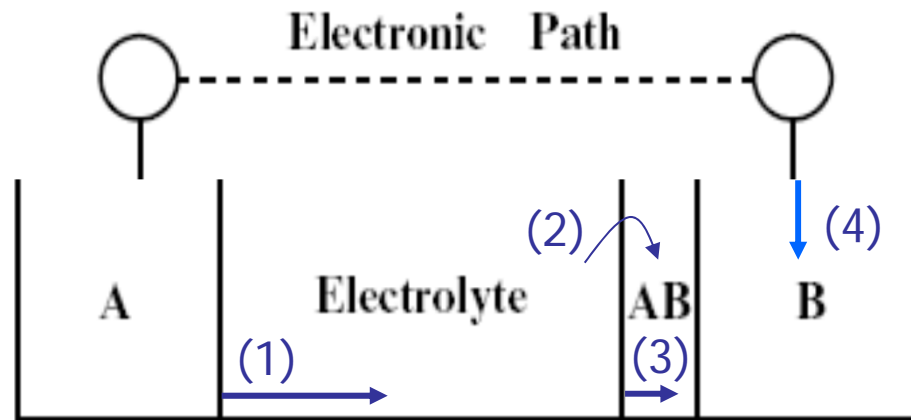
d) No clue

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Question kinetics 6

Current doesn't increase when increasing the overpotential
Electrolyte cannot provide Li-ions, mass transport limited => a) and b)

Different sources for the overpotential/internal resistance

$$\eta_{Total} = \eta_1 + \eta_2 + \eta_3 + \eta_4 \qquad r_{i,Total} = r_1 + r_2 + r_3 + r_4$$

(1) ionic conduction A^+ through the electrolyte
(2) Charge transport over the electrolyte-electrode interface
(3) solid state ionic conduction A or B
(4) electronic conduction

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Charge Transport, Ion transport electrode

Ionic transport through the electrodes

Diffusion of Li$^+$
Through a lattice:
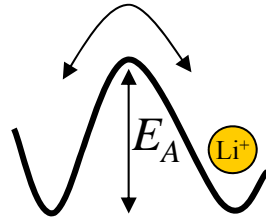
E_A: Activation barrier

Correlation time between jumps: $\tau_{Correlation} = \tau_0 e^{\frac{E_A}{kT}}$

ps Li-ion jump in TiO$_2$ (rutile)
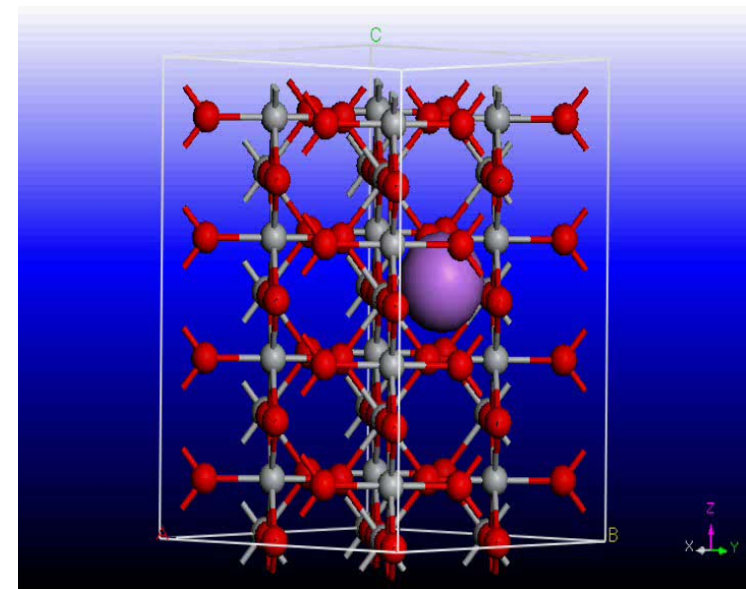
τ_0: attempt frequency, k: Boltzmann constant

Relation with diffusion coefficient:

$$D = \frac{nl}{\tau_{Correlation}}$$

n: number of jump directions
l: jump distance

$$D = D_0 e^{\frac{E_A}{kT}} \quad \text{where } D_0 = \frac{nl}{\tau_0}$$

Typical $D \sim 10^{-12}$ cm^2/s   (10^6 smaller than in the electrolyte!)

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Different sources for the overpotential/internal resistance

$$\eta_{Total} = \eta_1 + \eta_2 + \eta_3 + \eta_4 \qquad r_{i,Total} = r_1 + r_2 + r_3 + r_4$$


(1) ionic conduction A^+ through the electrolyte
(2) Charge transport over the electrolyte-electrode interface
(3) solid state ionic conduction A or B
(4) electronic conduction

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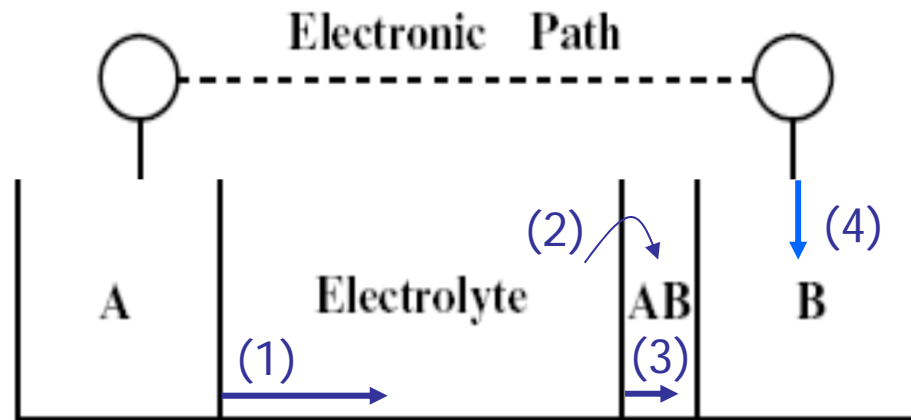
Charge Transport, Electronic transport

Electronic transport through the electrodes

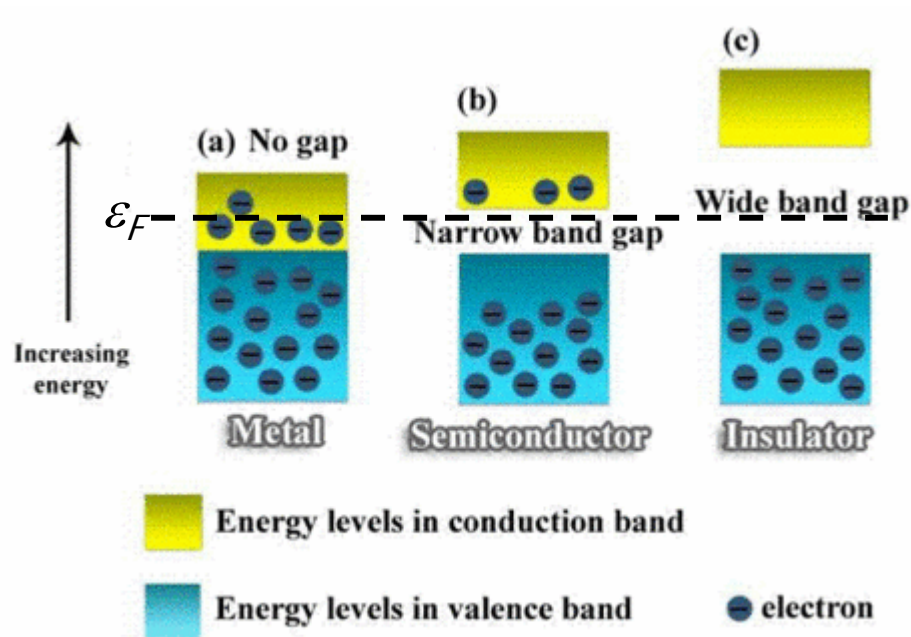Materials having vacancies for Li-ions are
typically semiconductors (no interstitial space
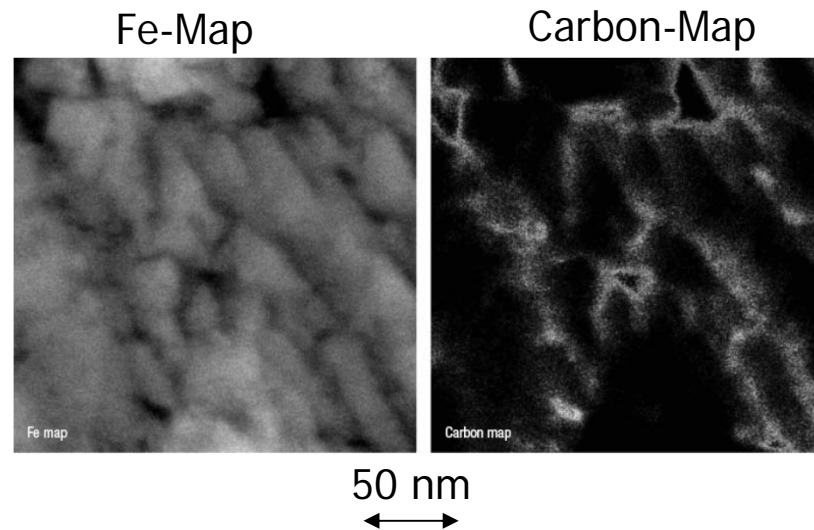in metals!), hence poor electronic
conductors.

Charge Transport, Electronic transport
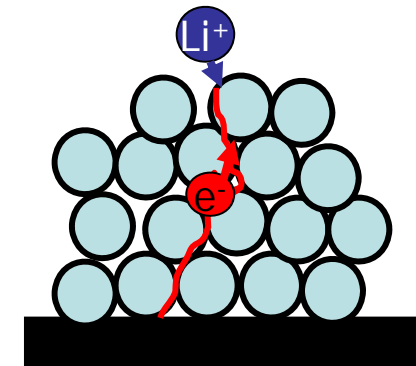
Improvement electronic conductivity:

Example $LiFePO_4$

Carbon coating nano particles (or coating with another conducting material):

Fe-Map   Carbon-Map

Fe map

Carbon map

50 nm

Note: the coating needs to be transparent for Li-ions!

Li+

e⁻

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Discussion Nature paper

LETTERS

Battery materials for ultrafast charging and discharging

Byoungwoo Kang[1] & Gerbrand Ceder[1]

The storage of electrical energy at high charge and discharge rate is an important technology in today's society, and can enable hybrid and plug-in hybrid electric vehicles and provide back-up for wind and solar energy. It is typically believed that in electrochemical systems very high power rates can only be achieved with super-capacitors, which trade high power for low energy density as they only store energy by surface adsorption reactions of charged species on an electrode material[1–4]. Here we show that batteries[5,6] which obtain high energy density by storing charge in the bulk of a material can also achieve ultrahigh discharge rates, comparable to those of supercapacitors. We realize this in LiFePO₄ (ref. 6), a material with high lithium bulk mobility[7,8], by creating a fast ion-conducting surface phase through controlled off-stoichiometry. A rate capability equivalent to full battery discharge in 10–20 s can be achieved.

Like any lithium battery material, LiFePO₄ absorbs and releases energy by the simultaneous extraction and, respectively, insertion of Li⁺ ions and electrons. Hence, the power capability of a lithium battery with this or other electrode materials will depend critically on the rate at which the Li⁺ ions and electrons can migrate through the electrolyte and composite electrode structure into the active electrode material. Strategies to increase the low rate performance of bulk LiFePO₄ have focused on improving electron transport in the bulk[9] or at the surface of the material[10,11], or on reducing the path length over which the electron and Li⁺ ion have to move by using nano-sized materials[12,13]. However, recent evidence indicates that Li⁺ transport along the surface may be as important as electron transport: whereas LiFePO₄ can in principle exchange Li⁺ ions with the electro-lyte on all surface facets, Li⁺ ions can only move into the bulk of the crystal in the [010] direction[7,8,14]. Hence, increasing diffusion across the surface towards the (010) facet should enhance rate capability.

In a departure from previous approaches[9–11], we have created a lithium phosphate coating on the surface of nanoscale LiFePO₄ and show that this results in extremely high rate performance. In particular, glassy lithium phosphates are well known to be good, stable Li⁺ conductors[15] and can be doped with transition metals to achieve elec-tronic conduction[16–18]. Supplementary Fig. 1 shows a small section of the calculated lithium–iron–phosphorus ternary phase diagram[19] equilibrated with an oxygen potential under reducing conditions, which represents typical synthesis conditions for LiFePO₄. Compositions with high phosphorus content on the Li₃O–P₂O₅ bin-ary edge are known to be very good glass formers with high lithium conductivity[20], and nitrogen-doped Li₃PO₄ has been used as a solid-state lithium electrolyte[21]. Typically, the glass-forming ability and lithium conductivity decrease with the presence of Li₂O. These glasses can dissolve a large quantity of transition-metal ions to increase the electronic conductivity[17,18], although such fully amorphous states with high levels of transition metals are usually only obtained by rapid quenching from the liquid state. Hence, the shaded area in the phase

diagram represents the optimal coating compositions with good lithium ion conductivity.

Our synthesis strategy has been to create an appropriate off-stoichiometry in the starting materials so that the coating constituents phase-separate from LiFePO₄ as it forms during the heat treatment, thereby creating the active storage material and coating in a single process. Here we describe results with an iron:phosphorus deficiency ratio of 2:1 (for example LiFe₁₋₂ᵧP₁₋ᵧO₄₋δ, y = 0.05), as indicated by arrow A in Supplementary Fig. 1. We note that the more common one-to-one iron:phosphorus deficiency (arrow B in Supplementary Fig. 1, equivalent to lithium excess[22]) creates a mixture of Li₃PO₄ and iron oxides, which are not likely to conduct well under the synthesis conditions used to prepare LiFePO₄.

LiFe₀.₉P₀.₉₅O₄₋δ was synthesized by ball-milling Li₂CO₃, FeC₂O₄·2H₂O and NH₄H₂PO₄ in appropriate amounts, heating the mixture at 350 °C for 10 h and then heating at 600 °C for 10 h under argon. X-ray diffraction (Fig. 1a and Supplementary Fig. 2) shows that despite the off-stoichiometric starting mixture, stoichiometric LiFePO₄ forms with lattice parameters (a = 10.3134 Å, b = 6.002 Å and c = 4.691 Å) very similar to those reported in the literature[23]. No crystalline Fe₂P can be observed in the X-ray pattern of the material synthesized at 600 °C, but a small amount of Fe₂P is present in the material synthesized at 700 °C (Fig. 1a). However, amorphous FeP or Fe₂P created by the reducing atmosphere cannot be excluded[24]. Mössbauer spectroscopy (Supplementary Fig. 4) indicates that apart from the major LiFePO₄ component, around 10% of the Fe is present in some other environment. The isomer shift (0.464 mm s⁻¹) and quadrupole splitting (0.798 mm s⁻¹) of this second component fall in the region of values given in the literature for Fe²⁺ in pyropho-sphate (P₂O₇-containing) glasses, although recent work[24] argues that iron monophosphides also give a Mössbauer signal in this range. To distinguish between the two possibilities, as-made material was discharged. The large discharge capacity found (Supplementary Fig. 5) is consistent with the presence of reducible Fe²⁺ rather than FeP in the material. Furthermore, in subsequent charge–discharge cycles we consistently find 15–18 mAh g⁻¹ capacity in the 3.2–2.0 V voltage window, in agreement with the ~10% proportion of iron found in the second Mössbauer component. Pyrophosphates are known to have somewhat lower potential than LiFePO₄[25].

Particle size as determined by scanning electron microscopy is ~50 nm (Fig. 1b). Transmission electron microscopy (Fig. 1c) shows a poorly crystallized thin layer on the surface. The thickness of this layer varies. Further evidence for the existence of the poorly crystallized layer is provided by X-ray photoelectron spectroscopy, which selectively analyses the surface of a material, and shows two different phosphorus 2p chemical states in our material. One state is close to the phosphorus 2p binding energy in LiFePO₄, but the second component is at higher energy. This is consistent with the presence of the (P₂O₇)⁴⁻ groups, where phosphorus has higher binding energy than LiFePO₄ (Fig. 2 and

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Question 1

The diffusion coefficient of Li-ion diffusion is 1 million times smaller in the electrode material (host material) compared to the electrolyte.

What would your solution be achieve faster (dis)charge rates?

a) Make the electrode more porous (more electrolyte, less storage material)

b) Reduce the size of the storage particles
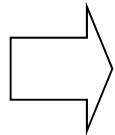
c) Increase the amount of carbon

d) no clue

$D = 10^{-6} \ cm^2/s$ $D = 10^{-12} \ cm^2/s$

Li$^+$

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Question 1

2d

Li$^+$
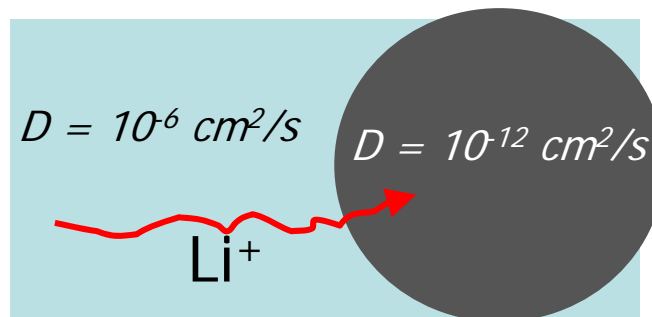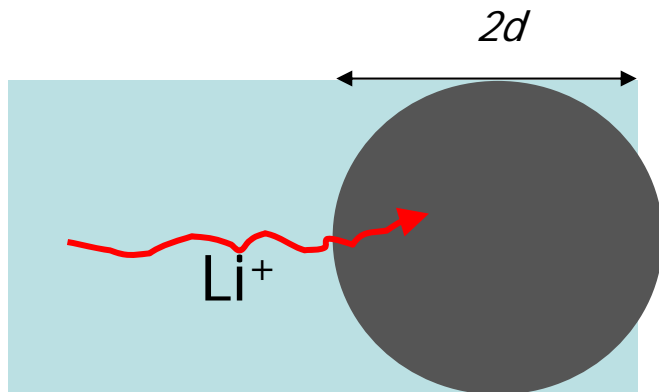
Diffusion distance: $\quad d \approx \sqrt{\pi D t}$

Diffusion time: $\quad t \approx \dfrac{d^2}{\pi D}$

$d = 1 \ \mu m$
$D = 10^{-12} \ cm^2/s$ $\quad \Longrightarrow \quad$ $t \sim 1 \ hour$

$d = 43 \ nm$
$D = 10^{-12} \ cm^2/s$ $\quad \Longrightarrow \quad$ $t = 6 \ s$

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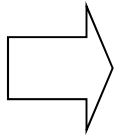
Nano sizing, pro's and con's

Disadvantages

Nano particles have low packing density (results in low energy density electrode) (-)

Shorter cycle life due to surface reactions that decompose the electrolyte (-)

Nano particles are less stable resulting in a shorter cycle life

Advantages

Supercapacitive behavior (charge in the double layer that can be released very quickly) leading to high power

Nano particles can host more strain resulting in a longer cycle life

Reactions that are otherwise impossible are possible when nano-structured (example: reconstitution-displacement reactions)

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Question 2

What charge transport mechanism does the paper claim to be rate limiting?

a) Electronic conduction in the electrode

b) Li-ion conduction through the electrolyte

c) Li-ion conduction over the surface of the electrode

d) Li-ion conduction through the electrode

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Question 3

What problems may be encountered charging a battery of an electrical car (~50 kWh) in 6 seconds

a) No problem

b) Heating up battery

c) Size of the electrical cables and connectors

d) Both b and c

e) No clue

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Question 3

50 kWh in 6 seconds

50 kWh ~ 180 MJ

180 MJ in 6 seconds = 30 MW (power of a small power plant)

At 4 Volts the charge that needs to pass is $180/4 = 45 \cdot 10^6$ Coulomb

In 6 seconds that leads to a current of $7.5 \cdot 10^6$ Amperes

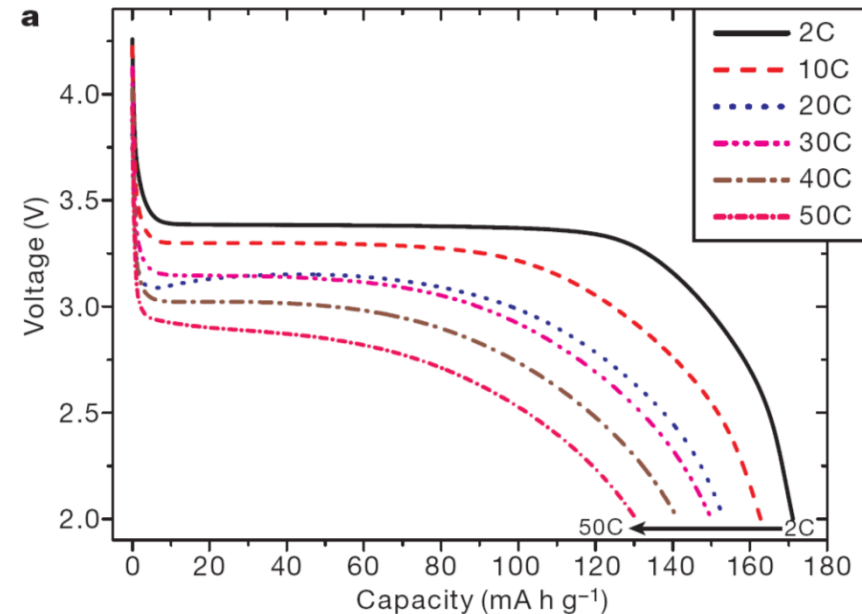=> Huge connectors

=> Large heat production in the battery

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Question 4

The voltage curves represent:
a) charging
b) discharging
c) no clue

The meaning of 30C is:
a) (dis)charging in 30 minutes
b) (dis)charging in 2 minutes
c) (dis)charging in 30 seconds
d) (dis)charging in 5 minutes
e) no clue

Question 4

The voltage curves represent:
a) charging
b) discharging
c) no clue

The meaning of 30C is:
a) (dis)charging in 30 minutes
b) (dis)charging in 2 minutes
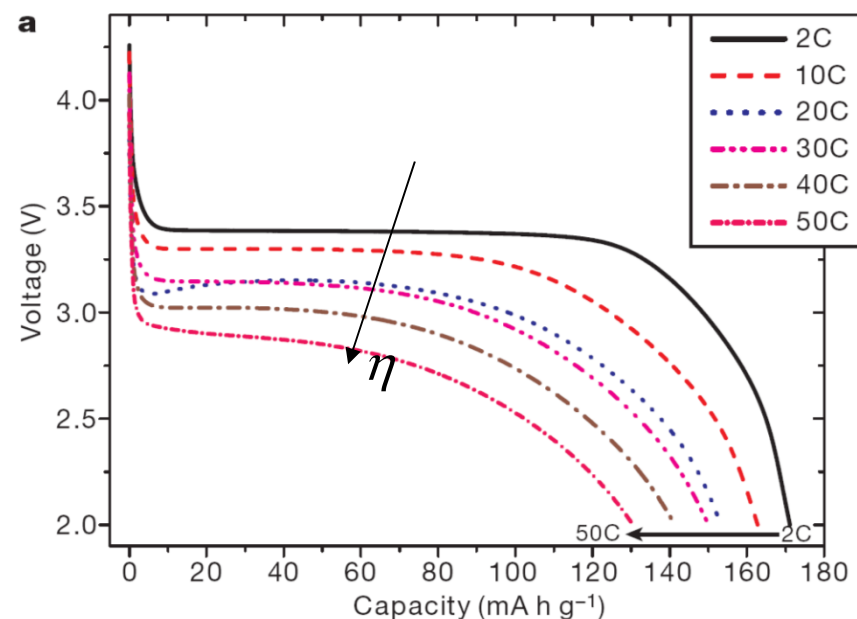c) (dis)charging in 30 seconds
d) (dis)charging in 5 minutes
e) no clue

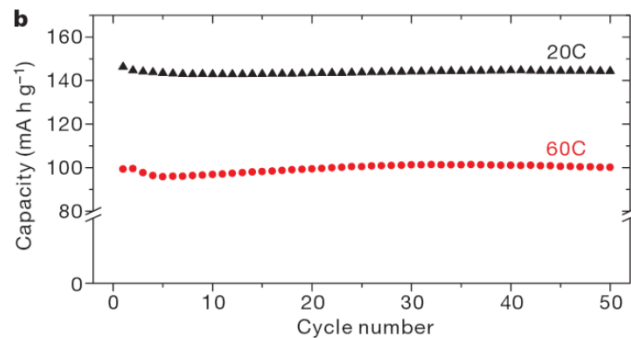Lower voltages with higher rates => discharge
Decreasing voltage => discharge
Meaning of 30C: thirty times the full capacity in 1 hour, so full capacity in 2 minutes => b) and b)

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Question 5

How will the electrode loading (mg/cm^2) will affect the charging time?

a) No effect

b) Increase charging time

c) Decrease charging time

d) no clue

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Question 5

Figure 3 | Discharge rate capability and capacity retention for LiFe$_{0.9}$P$_{0.95}$O$_{4-\delta}$ synthesized at 600 °C. a, Discharge rate capability after charging at C/5 and holding at 4.3 V until the current reaches C/60. C/n denotes the rate at which a full charge or discharge takes n hours. The loading density of the electrode is 3.86 mg cm^{-2}. At 2C, the capacity is close to the theoretical value. **b,** Capacity retentions when performing full charge–discharge cycles at constant 20C and 60C current rates for 50 cycles. The loading density of the electrode is 3.60 mg cm^{-2} for the 20C rate and 2.71 mg cm^{-2} for the 60C rate. The voltage window is approximately 2.5–4.3 V. The electrode formulation is active material (80 wt%), carbon (15 wt%) and binder (5 wt%).
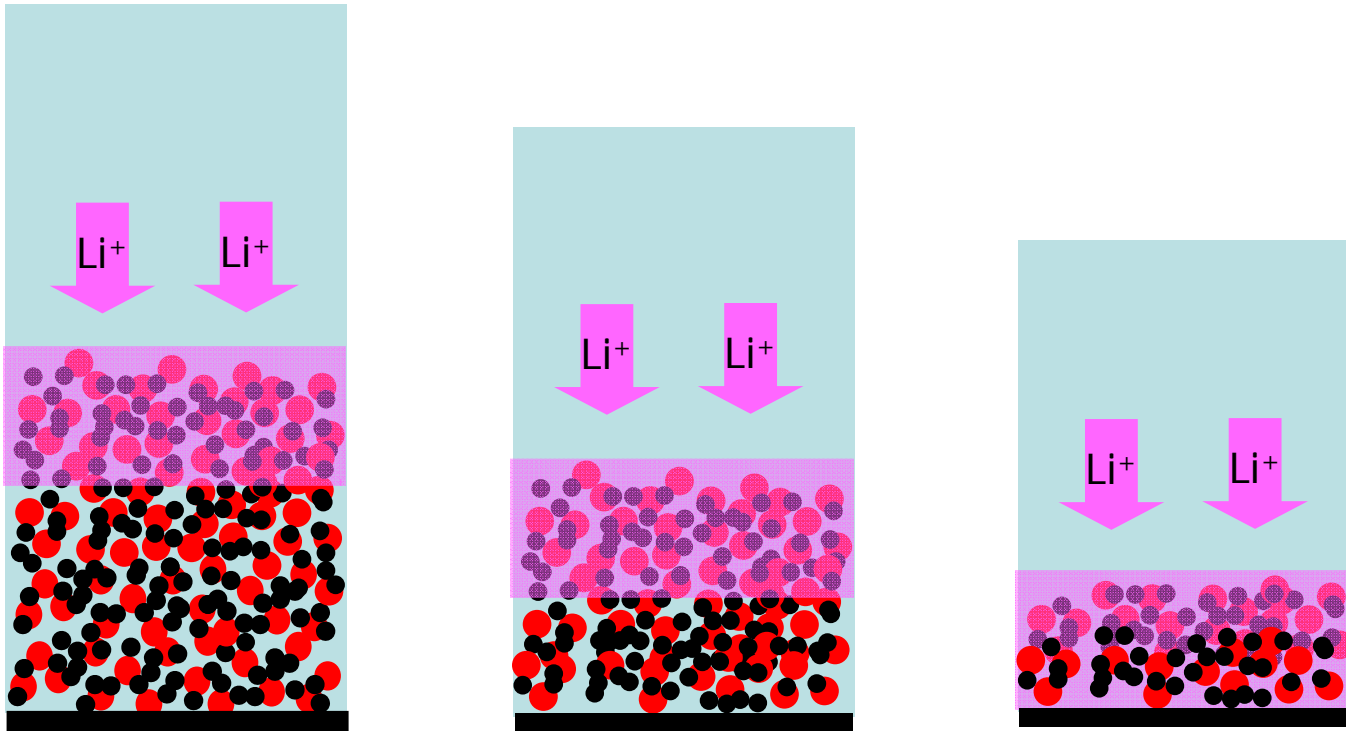
TUDelft
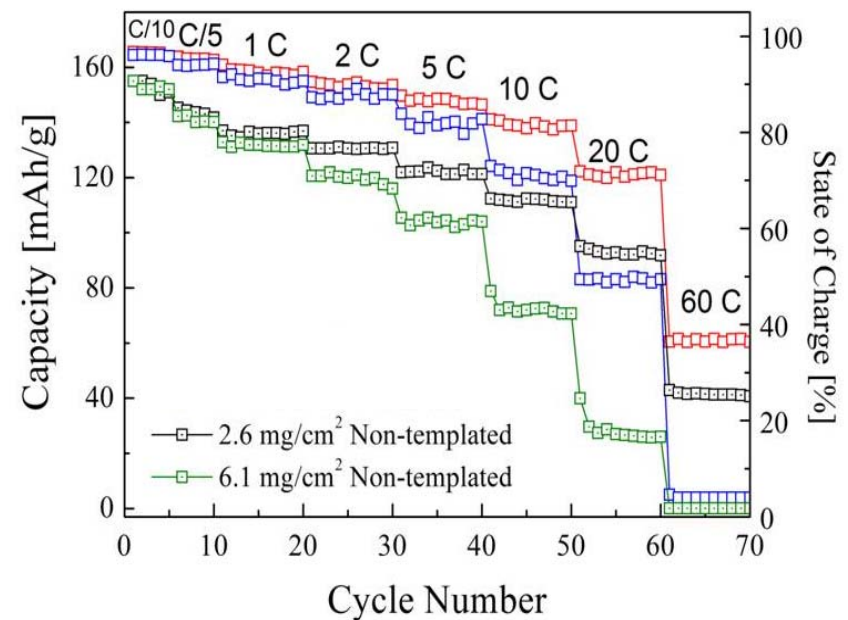
Question 5

Diffusion distance: $\quad d \approx \sqrt{\pi D t}$

Diffusion time: $\quad t \approx \dfrac{d^2}{\pi D}$

Question 6

Assume the charging time increases with increasing electrode loading (mg/cm^2) (equivalent with increasing electrode thickness). Which charge transport step do you conclude could to be rate limiting:

a) Electronic conduction through the electrode

b) Li-ion conduction through the electrolyte

c) Li-ion conduction over the surface of the electrode

d) Li-ion conduction through the electrode

e) Both a) and d)

f) No clue

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Question 6

Resistance that scales with the electrode thickness:

a) Electronic conduction through the electrode

b) Li-ion conduction through the electrolyte

c) Li-ion conduction over the surface of the electrode

d) Li-ion conduction through the electrode

e) Both a) and d)

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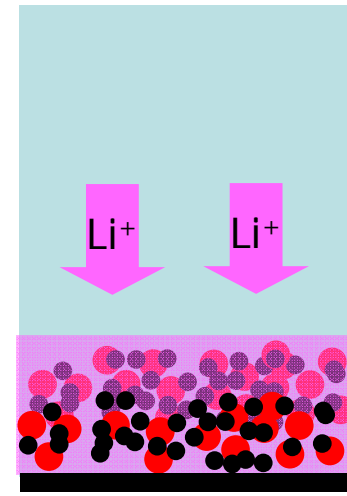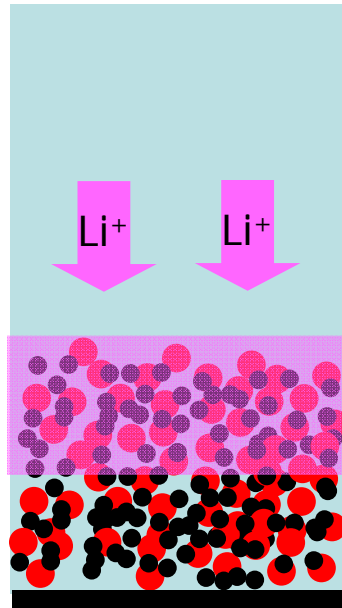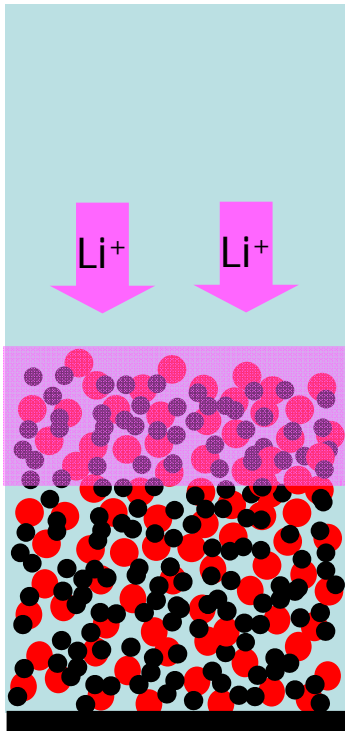
Energy density: amount of active material

~300 μm

~10 μm ① : Al Foil

~100 μm ② : Positive electrode

~20-25 μm ③ : Separator

~100 μm ④ : Negative electrode

~10 μm ⑤ : Cu Foil

~10 μm

~25 μm

~20-25 μm

~25 μm

~10 μm

20 March 2013   ~100 μm

~300 μm
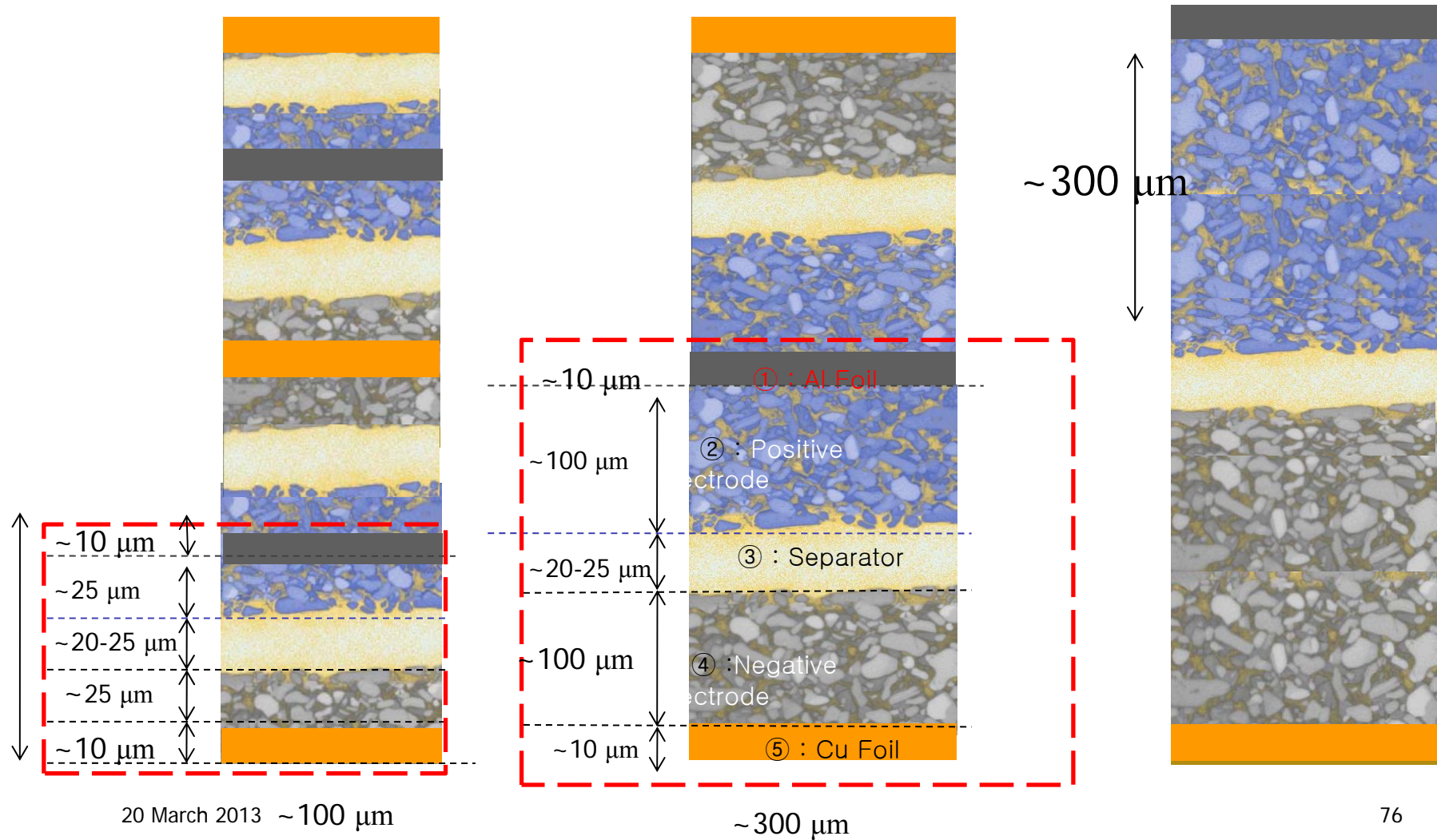
Increasing Energy Density

Ionic versus electronic conduction of the electrode

Increasing ionic resistance

Increasing electronic resistance

~3.4 mAh/cm²

~2.6 mAh/cm²

~1.7 mAh/cm²

~0.9 mAh/cm²

Time constant related to the (discharge time)

Increasing electrode loading/thickness

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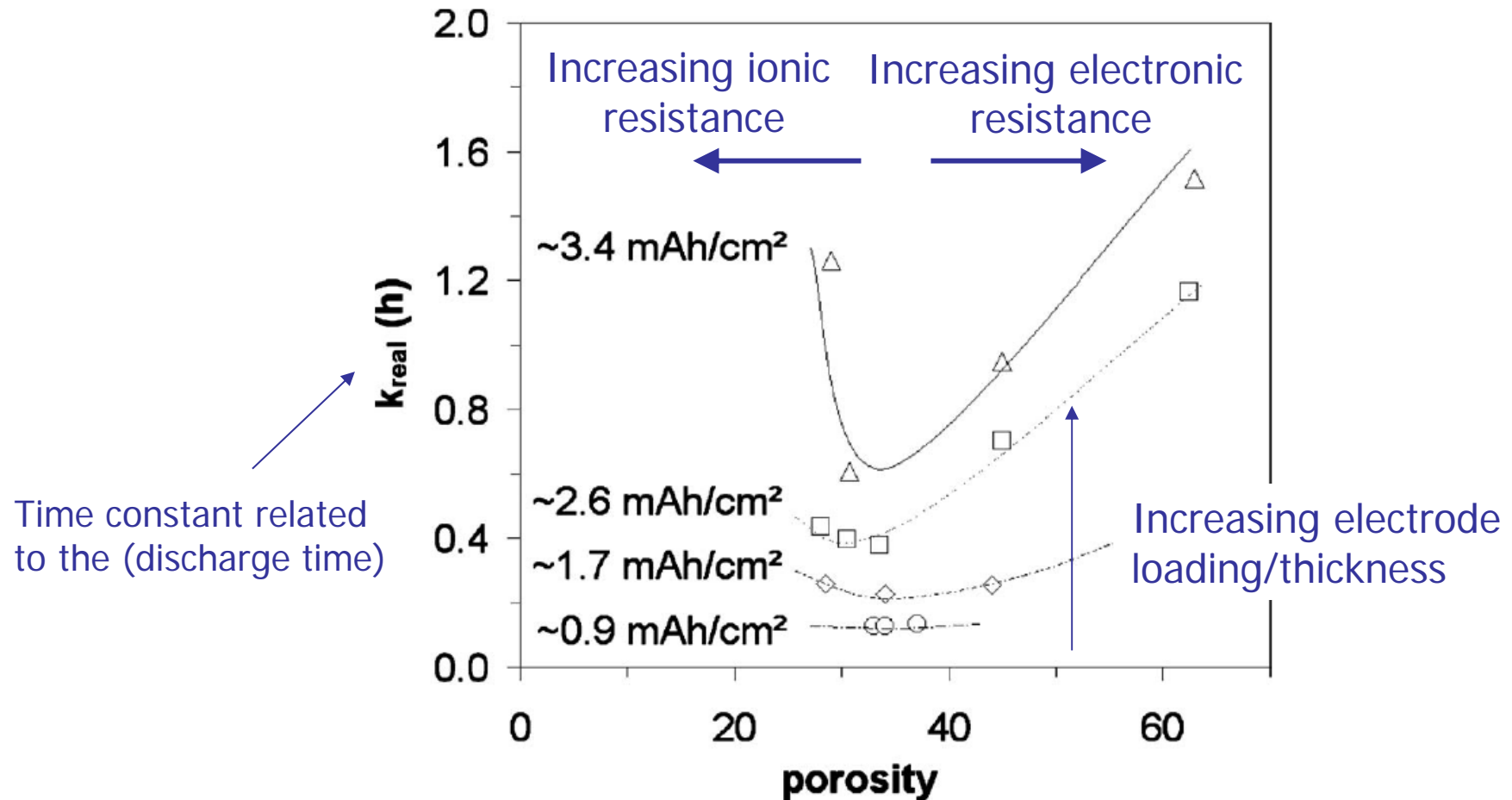
Question 7

By adding relatively more carbon black faster charging may be the result of:

a) Better electronic conduction in the electrode

b) better Li-ion conduction through the electrode

c) Less storage material ($LiFePO_4$) in the electrode

d) Both a) and c)

e) No clue

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Question 7

Yes: Better electronic conduction in the electrode => a)

But also Less storage material ($LiFePO_4$) in the electrode

Results in less Li-ion flux required through the electrode => c)

So answer d) both a) and c)

Li+ Li+

Li+ Li+
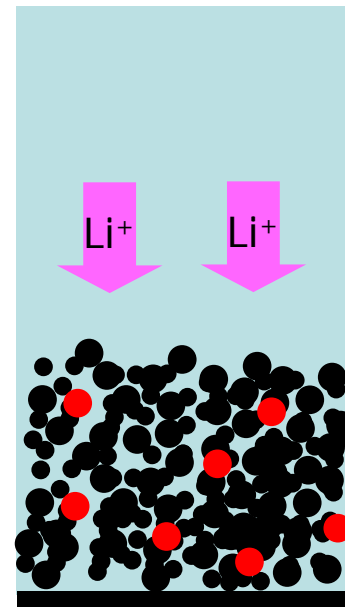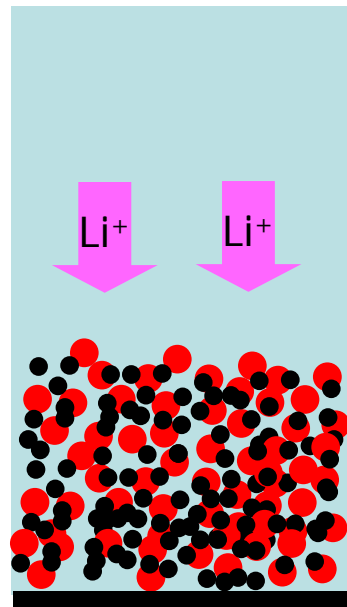
Note:
Low energy density!

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Conclusions

High power density $\longleftrightarrow$ High energy density

Thin electrodes   Thick electrodes
Porous electrodes   Dense electrodes
Nano structured electrodes   Large particles
(low packing density)   (large packing density)
"Diluted" electrodes   Concentrated electrodes
(carbon addition)   (pure storage material)

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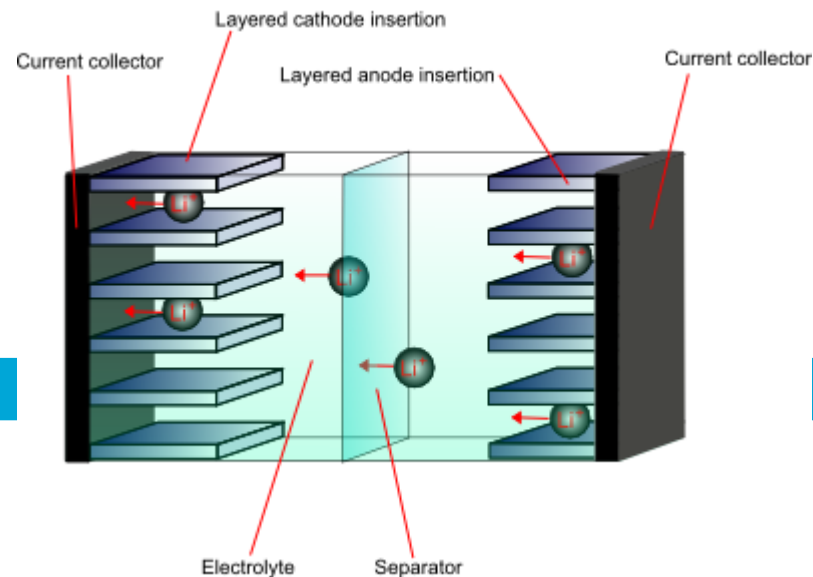
Improving the electrode morphology
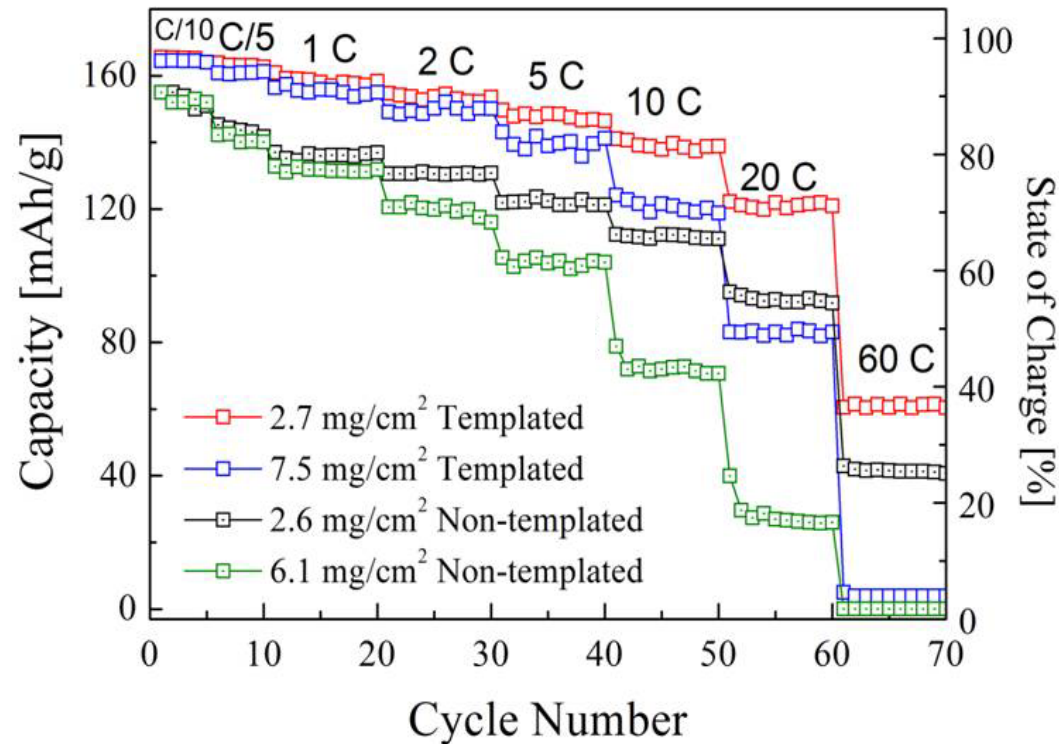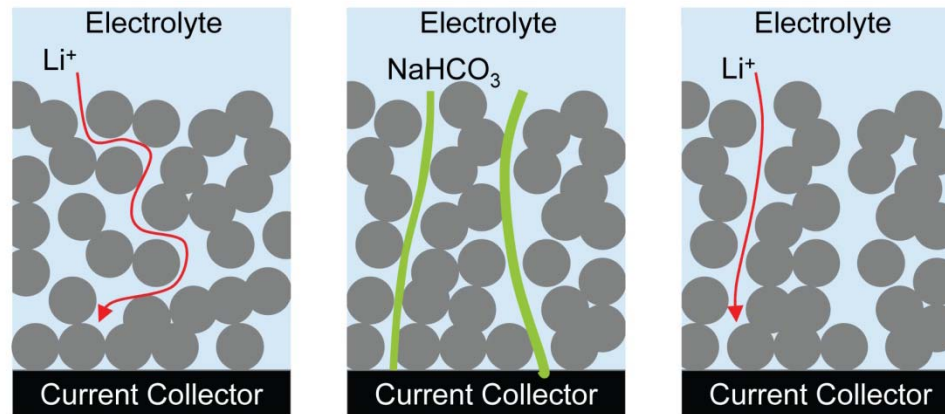
Summarize charge transport

(1a) Ionic transport through electrolyte: No problem

(1b) Ionic transport through the electrolyte in the electrode   In practice rate limiting
                                                                                          Requires smart electrode design

(2)   Charge transfer from electrolyte to the electrode: Usually not rate limiting in Li-ion
                                                                                          batteries, it usually is in other
                                                                                          types of batteries.

(3)   Ionic transport through the electrodes: Often Rate limiting, not for small
                                                                                          particles!

(4)   Electronic transport through the electrodes: Often Rate limiting, can be
                                                                                          solved with carbon

Program Batteries

Lecture 1: Feb 27	History, Applications, basic Electrochemistry and thermodynamics of batteries: Redox reactions, Gibbs free energy, chemical potential, Nernst.
Lecture 2: March 6	Solid state electrode reaction mechanisms, phase diagrams, phase rule, Gibbs Free energy, voltage profiles, capacities and energy densities. Li-ion batteries
Lecture 3: March 13	Continue topics Lecture 2. Electrolyte stability: Pourbaix diagram, band structure solids, Cycle life.
Lecture 4: March 20	Kinetics, Buttler-Volmer, diffusion, solid state diffusion Discussion on Science paper 6 seconds discharge.

Lecture 5: Super capacitors
March 27

Future large energy density systems: Li-air
                                        Li-sulfur

Batteries for large scale applications: Lead-acid
                                           Li-ion
                                           Flow-cells
                                           Sodium aqueous batteries

Costs and Performance comparison batteries/systems

To do for next week

Read review Li-air and Li-S (BB)

Collect questions for the last battery lecture